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A

MANUAL OF CHEMISTRY,

ON THE
BASIS OF PROFESSOR BRANDE'S;

CONTAINING

THE PRINCIPAL FACTS OF THE SCIENCE, ARRANGED IN THE
ORDER IN WHICH THEY ARE DISCUSSED AND
ILLUSTRATED IN THE LECTURES

AT

HARVARD UNIVERSITY, N. E.; THE UNITED STATES MILITARY ACADEMY, WEST
POINT; BROWN UNIVERSITY, AMHERST, AND SEVERAL OTHER
COLLEGES IN THE UNITED STATES.

COMPILED FROM THE WORKS OF

THE MOST DISTINGUISHED CHEMISTS.

DESIGNED

AS A TEXT BOOK FOR THE USE OF STUDENTS, AND PERSONS
ATTENDING LECTURES ON CHEMISTRY.

THE SECOND EDITION,

COMPREHENDING THE RECENT DISCOVERIES, AND ILLUSTRATED WITH
NINE PLATES AND SEVERAL ENGRAVINGS ON WOOD.

BY JOHN W. WEBSTER, M. D.

Erving Professor of Chemistry and Mineralogy in Harvard University.

Boston :

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1828.

20

DISTRICT OF MASSACHUSETTS, *to wit*:

District Clerk's Office.

BE IT REMEMBERED, That on the nineteenth day of December, A. D. 1828, in the fifty-third year of the Independence of the United States of America, RICHARDSON & LORD, of the said district, have deposited in this office the title of a book, the right whereof they claim as proprietors, in the words following, *to wit*:

"A Manual of Chemistry, on the basis of Professor Brande's; containing the principal facts of the Science, arranged in the order in which they are discussed and illustrated in the Lectures at Harvard University, N. E.; the United States Military Academy, West Point; Brown University, Amherst, and several other colleges in the United States. Compiled from the works of the most distinguished Chemists. Designed as a text book for the use of students and persons attending Lectures on Chemistry. The Second Edition, comprehending the recent discoveries, and illustrated with nine plates and several engravings on wood. By John W. Webster, M. D. Erving Professor of Chemistry and Mineralogy in Harvard University."

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JAMES JACKSON, M. D.

*HERSEY PROFESSOR OF THE THEORY AND PRACTICE OF PHYSICK,
IN HARVARD UNIVERSITY,*

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OF

THE COMPILER.

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TO THE SECOND EDITION.

THE basis of this work is the excellent Manual of Professor Brande; it contains all the strictly chemical part of that volume, with such modifications as the progress of chemistry has rendered necessary. All that part of Professor Brande's work which relates to Mineralogy and Geology has been omitted; its place being supplied with more full descriptions of the chemical properties of individual substances, and with more ample directions for the practical student.

The object of the compiler having been to place in the hands of students of chemistry a compendium of the leading facts and opinions upon which the science is founded, he has endeavoured not to limit the student to any particular theories, but to sketch the outlines of those of the most eminent writers, leaving to the teacher the discussion of their various merits. In most cases the extracts from other writers have been made without alteration, except where it was required to give a greater degree of uniformity to the phraseology. The extracts are designated by the first letter of the writer's name, and references are given to the volume and page for the convenience of those who may wish to consult the original memoirs.

Some of the statements in regard to individual substances will be found to differ occasionally in different parts of the work. This has arisen from the circumstance that new experiments and new views have been continually appearing in the Scientific Journals received from abroad, and the insertion of these has been deemed necessary to fulfil the object of the work.

Several alterations and improvements have been made in the present edition. Many valuable practical directions have been introduced from Mr Faraday's late work on *Chemical Manipulation*, and the section on the Analysis of Minerals from Dr Turner's *Elements* has been substituted for that originally inserted in the first edition. Several useful *tables* and a

description of Dr Wollaston's Scale have been placed in an appendix. In the ADDENDA will be found an account of such discoveries, as could not, from the date of their publication, be noticed in their proper places.

To the gentlemen who have aided the compiler by their advice and assistance, who have kindly pointed out errors of the press, and suggested improvements, especially Professor Torrey, and Lieuts. Hopkins and Mather of the U. S. Military Academy, Samuel Moore, Esq. Director of the U. S. Mint, and others, he begs leave thus publicly to express his obligations.

The communication of any errors which have escaped notice in the present edition, will be gratefully received.

Cambridge, Dec. 1828.

NOTE.

The letter D refers to Davy's *Elements of Chemical Philosophy*.

H " Henry's " *Chemistry*.

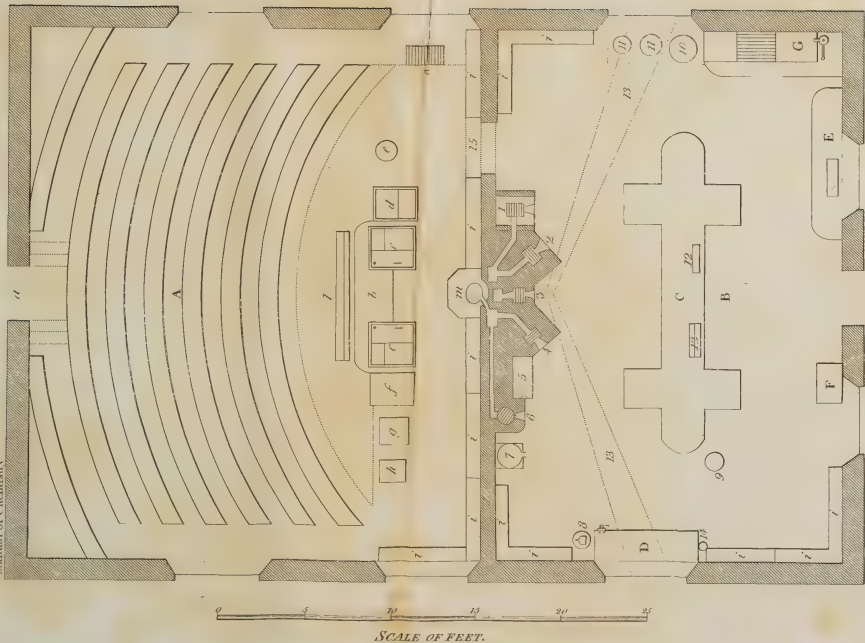
U " Ure's *Dictionary of Chemistry*.

M " Murray's *System of* do.

T " Thomson's do. do. and *Attempt to establish the first Principles of Chemistry by Experiment*, and Turner's *Elements*.

F " Faraday's *Chemical Manipulation*.





SCALE OF FEET.

EXPLANATION OF PLATES VIII. AND IX.

Plate VIII. is a ground plan of the Chemical Laboratory and Lecture Room in Harvard College.

A Is a part appropriated to the audience, *a* entrance.

B Is the body of the laboratory, *b* lecture table containing *c c* cisterns for gases furnished with stop-cocks projecting through the covers, which can be removed when large jars are to be filled. To the stop-cocks flexible tubes may be connected to form the oxy-hydrogen blow-pipe, the tubes communicating with a jet formed of two cones, see section (fig. 16, pl. 9.) *d*, pneumatic table, (fig. 73, pl. 3.) *e*, furnace stove. *f*, mercurial cistern, (pl. 3, fig. 76.) *g*, Table with electrical machine. *h*, Table with air pump. *iiii*, Cases for apparatus. *k*, Large Calorimotor. *l*, Deflagrator. *m*, Small universal furnace.

C Table with drawers in the form of a double cross, for the general uses of the laboratory.

D Table with vice, anvils, mortars, files, &c.

E Table with balances in glazed cases.

F Smaller table.

G Sink, pump, bottle racks, &c.

1, Sand bath. 2, a furnace for the production of oxygen and other gases. 3, Wind furnace with air flues (13) under the floor of the laboratory. See Section (pl. 9, fig. 2). 4, Assay furnace. 5, Forge. 6, A copper boiler, (plate iv. fig. 97,) &c. 7, Refrigeratory. 8, Anvil. 9, Universal furnace, (fig. 3, pl. 9). 10, Copper gasometer, from which tubes pass into the lecture room. 11, Gas holders. 12, Racks, with test tubes, &c. (see figs. 17 and 18, pl. 9). 14, Large Mortar. 15, Door communicating with the lecture room.

Plate IX. exhibits sections of the furnaces, and views of several useful parts of the apparatus not described in the body of the work,

Fig. 1 is a section of the sand furnace, 1 Pl. 8.

2 is a ditto of the wind ditto, 3 Pl. 8. *a* is a flue communicating with the exterior of the building for the admission of cold air to the fire place. *b* the ash-pit. *c* a plate of iron to direct the current of air through the grate *d*. *e* a moveable cover. *f* the chimney.

3 Knight's improved Black's portable furnace. *a* iron kettle to contain sand, which fits into the opening at the top of the furnace. *b* a cover. *c* aperture to which there is a corresponding one on the opposite side for the admission of a tube to pass through the furnace.

4 A cupelling or enamelling furnace. *a* the ash-pit. *c* the grate. *d* the muffle. *e* the opening for introducing the muffle. *f* the chimney. *g* the cover.

5 A portable furnace of earthen ware which may be placed on a table. These furnaces are manufactured by Mr Miller, of Philadelphia, and are convenient for many purposes.

6 A filtering bag. 7, 8 and 9 Evaporating basins.

10 A platinum crucible and cover. 11 Skittle shaped crucible. 12 Covered do. 13 An iron ring covered with cloth for supporting retorts.

14 A small Calorimotor for exploding gases by the ignition of a fine platinum wire, in the glass vessel fig. 15. The vessel having been filled with the mixed gases, by means of the air-pump, is placed upon the cross bar of the Calorimotor and the thick wires *a a*, which are connected by the fine platinum wire *b*, are brought in contact with the poles of the calorimotor by means of the screws *a a*, fig. 14. A copper vessel, coated within and without with cement, is represented beneath the plates of the instrument. The contact being made, the copper vessel containing the liquor is raised until the plates are immersed, when the small wire *b* is instantly ignited. For a full account of this most convenient apparatus see Dr Hare's description in the American Journal of Science, vol. x. 67.

16 Jet for the oxy-hydrogen blow-pipe, formed of two cones, with an intervening space. *a* an internal screw communicating with the space *between* the cones; *b* a similar screw communicating only with the *inner* cone. The gases issue at the orifices *c*, and either gas may be made to surround the other.

17 A filtering stand.

18 A rack for test-glasses.

19 A small anvil.

20 Alcohol blow-pipe, *a* a spherical copper vessel furnished with a safety valve *b*; the alcohol being made to boil by the flame of the lamp *c*, its vapour passes out through the jet *d*, just above the wick of the lamp, which inflames it.

21 Is the muffle represented at *d*, fig. 4.

22 Precipitating jars.

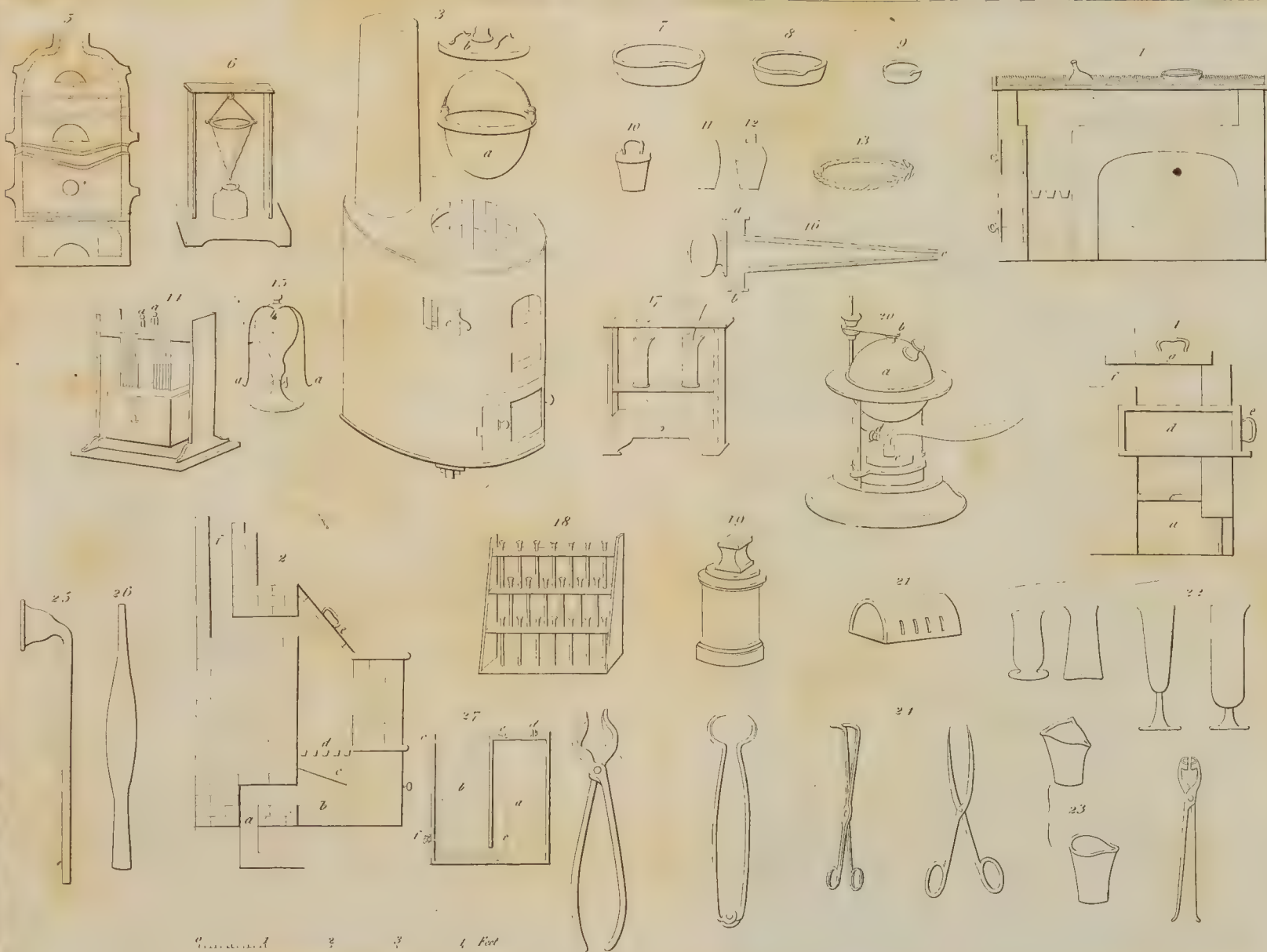
23 Hessian crucibles.

24 The principal varieties of tongs useful in the laboratory.

25 A long funnel for introducing liquids into retorts without soiling their necks.

26 An adopter for lengthening the necks of retorts.

Fig. 27, is a vertical section of one of the cisterns within the lecture table (*c c* of plate viii.) One half of each is covered so as to form an air-tight box, the partition, which divides the cistern and forms one side of the box, descending to within two inches of the bottom. *d, e* are two air-cocks, one vertical, the other horizontal. The air-cocks being open the cistern is filled with water, they are then closed, and the cock at *f* opened which allows the water to escape till the lower edge of the partition is nearly uncovered; the water remaining within the box *a*. A tube *c* passes down the side of the cistern and along its bottom, turning up under the partition; through this any gas may be introduced, which, rising, displaces the water in *a*, causing it to pass into the other part of the cistern *b*. When the gas is wanted for use it is only necessary to open one of the air-cocks *e, d*, and the water in *b* falling expels the gas from *a* through it, where it may be received in air jars placed over the horizontal cock, or be allowed to pass into a tube screwed upon *d*.



1. Foot 2. 3. 4. Foot

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ERRATA.

Page 2d, after "Electricity" insert "4 Light."

26, line 19, for "1,25" read "0,125."

79, " 14, for "detonaton" read "detonation."

118, dele "plate 2d" in the margin.

217, line 24, for "(100)" read "(790)."

254, in the table for "*Alumium*" read "aluminum."

295, line 24, for "hydrogen gas" read "Sulphuretted hydrogen."

318, note, 2d line for "see analysis of minerals" read "*Quart. Jour.* vi.

316, and *Edin. Philos. Jour.* vii. 108."

319, in the margin for "alumina" read "aluminum."

372, in 2d line of the note, for "matrice" read "matrass."

373, line 28, for "00" read "100."

456, " 14, for "minerel" read "mineral."

500, " 11th from bottom, for "camposition" read "composition."

522, " 26, for "Selerotium" read "Sclerotium."

MANUAL OF CHEMISTRY.

CHAPTER I.

OF THE POWERS AND PROPERTIES OF MATTER, AND OF THE GENERAL LAWS OF CHEMICAL CHANGES.

1. It is the object of Chemistry to investigate all changes in the constitution of matter, whether effected by heat, mixture, or other means.* Object of
Chemistry.

Most of the substances belonging to our globe are constantly undergoing alterations in sensible qualities, and one variety of matter becomes as it were transmuted into another. Such changes, whether natural or artificial, whether slowly or rapidly performed, are called chemical; thus the gradual and almost imperceptible decay of the leaves and branches of a fallen tree exposed to the atmosphere, and the rapid combustion of wood in our fires, are both chemical operations. The object of chemical philosophy is to ascertain the causes of all phenomena of this kind, and to discover the laws by which they are governed.† The ends of this branch of knowledge are the application of natural substances to new uses, for increasing the comforts and

* The word *Chemistry* seems to be of Egyptian origin, and to have been originally equivalent to our phrase *natural philosophy* in its most extensive sense. In process of time it seems to have acquired a more limited signification, and to have been confined to *the art of working metals*. In the third century, we find it used in a much more limited sense, signifying the *art of making gold and silver*. Those who professed this art gradually assumed the form of a sect, under the name of Alchemists; a term which is supposed to be merely the word *chemist*, with the Arabian article *al* prefixed. The great object of the alchemists was to find out the means of converting the baser metals to gold, and the grand instrument by which this was to be effected was the philosopher's stone. T. i. 19.

† Chemistry is the science which treats of those events and changes in natural bodies, which are not accompanied by sensible motions. T. i. 18.

It is the object of Chemistry, to discover and explain the changes of composition that occur among the integrant and constituent parts of different bodies. H. i. 12.

Chemistry investigates those actions which are exerted between the minute particles of matter, at distances altogether imperceptible, causing them to pass into new arrangements and combinations, whence the properties of the bodies acted on are changed, their constitution is subverted, and new substances are formed. In conformity to these views the science may be defined, as that which investigates the combinations of matter and the agencies of those general powers whence these combinations are established and subverted. M. i. 1, 4.

Foundations
of chemical
philosophy.

enjoyments of man, and the demonstration of the order, harmony, and intelligent design of the system of the earth.

The foundations of chemical philosophy are observation, experiment, and analogy. By observation, facts are distinctly and minutely impressed on the mind. By analogy, similar facts are connected. By experiment, new facts are discovered; and in the progression of knowledge, observation, guided by analogy leads to experiment, and analogy confirmed by experiment, becomes scientific truth. D. 1, 2.*

Arrange-
ment.

2. The general range of Chemistry, is so extensive, and the individual cases requiring explanation, are so numerous, that *arrangement* is of the first consequence to its successful study; and in the present state of our knowledge, it will be found most convenient to begin with the discussions relating to the general powers or properties of matter, and afterwards to proceed to the examination of individual substances, and to the phenomena which they offer when presented to each other under circumstances favourable to the exertion of their mutual chemical agencies.

3. The powers and properties of matter, connected with chemical changes, may be considered under the heads of

1. Attraction.

2. Heat.

3. Electricity.

SECTION I. *Attraction.*

Attraction at
sensible dis-
tances.

4. ALL bodies composing the material system of the universe have a mutual tendency to approach each other, whatsoever may be the distances at which they are placed. The operation of this force extends to the remotest parts of the planetary system, and is one of the causes that preserve the regularity of their orbits. The smaller bodies, also, that are under our more immediate observation, are influenced by the same power, and fall to the earth's surface, when not prevented by the interference of other forces. From these facts the existence of a

* To give an instance—Whoever will consider the slender green vegetable filaments (*conferva rivularis*) which in summer exist in almost all streams, lakes, or pools, under the different circumstances of shade and sunshine, will discover globules of air upon the filaments exposed under water to the sun, but no air on the filaments that are shaded. He will find that the effect is owing to the presence of light. This is an *observation*; but it gives no information respecting the nature of the air. Let a wine glass filled with water be inverted over the *confervæ*, the air will collect in the upper part of the glass, and when the glass is filled with air, it may be closed by the hand; placed in its usual position, and an inflamed taper introduced into it, the taper will burn with more brilliancy than in the atmosphere. This is an *experiment*. If the phenomena are reasoned upon and the question is put, whether all vegetables of this kind, in fresh or in salt water, do not produce such air under like circumstances, the inquirer is guided by *analogy*; and when this is determined to be the case by new trials, a *general scientific truth* is established; that all *confervæ* in the sunshine produce a species of air that supports flame in a superior degree; which has been shown to be the case by various minute investigations. D. 1, 2, 3.

property has been inferred, which has been called *attraction*, or more specifically, the *attraction of gravitation*. Its nature is entirely unknown to us. The attraction between these bodies takes place at sensible distances ; it exists in all known forms of matter ; and it acts upon them directly as the mass, and inversely as the square of the distance.

5. From reviewing bodies in the aggregate, we may next proceed to contemplate them as composed of minute particles. Of the nature of these particles we have no satisfactory evidence. In simple bodies the particles must be all of the same nature, or *homogeneous*. In compound bodies, we are to understand by the term *particles*, the smallest parts into which bodies can be resolved without decomposition. The word *atom* has of late been revived, to denote both these kinds of particles ; and we may therefore, speak with propriety of *simple atoms* and of *compound atoms*. When two atoms of different kinds unite to form a third or compound atom, we may term the two first *component atoms* ; and if these have not been decomposed, they may be called *elementary* or *primary atoms*. H. 1, 28.

6. Attraction is exerted between these minute particles, or atoms, when they are placed in apparent contact, and is effective only at insensible distances. This has been called *contiguous attraction*, and has been distinguished as it is exerted between particles of matter of the *same* kind, or between particles of a *different* kind. When the particles of the same kind are united to form an aggregate or mass, they are sometimes said to be united by the *affinity of aggregation*, the *cohesive affinity*, or by that force or power termed *cohesion*.

7. The attraction which is exerted at insensible distances, preserves the form, and modifies the texture of solids, gives a spherical figure to fluids, causes the adhesion of surfaces, and influences the mechanical characters of bodies.

8. In solids its force is exerted with the greatest intensity ; in liquids it acts with much less energy ; and in aeriform bodies it is doubtful if it exists at all : thus water in a solid state has considerable cohesion, which is much diminished when it becomes liquid, and is entirely destroyed as soon as it is changed into vapour.

The force of cohesion in solid bodies is measured by the weight necessary to break them, or rather to pull them asunder.

9. In liquids the force of cohesion is demonstrated by the spherical figure which they assume, when suffered to form drops. The drop is spherical because each particle of the fluid exerts an equal force in every direction, drawing other particles towards it on every side, as far as its power extends. To the same cause is owing the property possessed by all liquids of remaining heaped up above the brims of the vessels which contain them.

The force of cohesion varies in different liquids, as it does in different solids and hence the size of their respective drops must also vary.

Heterogeneous, or chemical attraction.

10. When attraction operates upon *dissimilar* particles, it produces their union, giving rise to new and infinitely varied productions. It is this kind of attraction which is distinguished as *heterogeneous*; it is also called Chemical attraction, or Affinity.

Results.

11. The results of attraction, as relating to the texture and forms of matter, are influenced by the circumstances under which it has taken place. Sometimes the particles are, as it were indiscriminately collected; and at others they are beautifully arranged, giving rise to regular and determinate figures: in this case, bodies of the same composition almost invariably affect the same form; hence we are often enabled to infer the composition of a substance from accurate inspection of its external or mechanical characters.

Crystals.

12. The regular polyedral solids thus resulting from the influence of attraction upon certain kinds of matter, are usually called *crystals*;^{*} and the bodies are said to be susceptible of *crystallization*.

Conditions for crystallization in general.

13. To enable the particles of bodies to assume that regular form which crystals exhibit, it is obvious that they must have freedom of motion; and accordingly the first step towards obtaining a body in its crystalline form, is usually to confer upon it either the liquid or aeriform state. This is effected by solution, or by exposure to heat.

Exceptions.

14. The experiments of Mr Watt† and others have shown that under some circumstances a body not crystalline may become so without changing its state of solidity. The crystallization of cooling basalt, of heated glass, or even the spontaneous change of brass wire, which in a few years becomes brittle, are all effects of this kind.

Solution.

15. The term, *solution*, is applied to a very extensive class of phenomena. When a solid disappears in a liquid, if the compound exhibit perfect transparency, we have an example of solution. The expression is applied both to the *act* of combination, and to the *result* of the process. When common salt, such as is used in cookery, is agitated with water, it disappears; in other words, its solution takes place; and we also term the liquid which is obtained, a *solution of salt in water*. This is one of the simplest cases that can be adduced of the efficiency of chemical attraction; for solution is always the result of an attraction or affinity, between the fluid and the solid which is acted upon, feeble it is true, yet sufficient in force to overcome the cohesion of the solid. The affinity continues to act until at length a certain point is attained, where the affinity of the solid and fluid for each other is overbalanced by the cohesion of the solid, and the solution cannot be carried farther. This point is called *saturation*, and the fluid obtained is termed a *saturated solution*. H. 1. 31.

Saturation.

^{*} From Κρύσταλλος, Ice.

† Phil. Trans. 1804, p. 282.

16. The particles of the salt may be regarded as disposed at regular distances throughout the fluid; and if the quantity of water be considerable, the particles will be too far asunder to exert reciprocal attraction; in other words, they will be more powerfully attracted by the water than by each other. If we now slowly get rid of a portion of the water, the saline particles will gradually approach each other, and they will aggregate according to certain laws producing a regular solid of a cubic form.

17. In addition to what has been stated (13) there are two other great and general objects to be gained by solution, which render it a process of constant occurrence in the laboratory. The first is that of preparing substances for the exertion of chemical action. The second is that of separating one substance from another; this being continually effected by the use of such fluids as have a solvent power over one or more of the substances present. Water is the great solvent whose aid is first to be called in; others are to be resorted to only when that is insufficient. So general and important is its use, that in speaking simply of the solubility of a body, water is always understood to be referred to. The solubility of a body may be tried by suspending a piece of it in a glass of clean undisturbed water; if it be soluble a descending current will be seen to fall from it, and be visible upon looking through the water horizontally. If it fall rapidly and in dense striæ, it will indicate rapid solubility, and the formation of a dense solution; if it fall in a very narrow stream, it will indicate only moderate or slight solubility; and by its descending rapidly or in a slow broad stream, or by resting about the substance, a judgment may be made of the comparative density of the solution produced. If no descending current appear, nor any fluid round the substance of a refractive power or colour different to that of the water, then the body must be very nearly if not quite insoluble at common temperatures.

Other objects
of solution.

Solubility,
how tried.

If the substance appear to be insoluble, or if it be necessary to know whether it be soluble in alcohol, ether, oils, or any other body, for the purpose of selecting a solvent from among them, a portion should be pulverized finely, and introduced into a small tube with a little of the fluid to be tried, and heated; if the substance disappear, it is of course soluble. But if it be supposed to be a mixed body, and partly soluble, though not altogether so, then the presumed solution should be poured from the tube into an earthenware or platinum capsule, (pl. ix. figs. 8, 9.) and evaporated carefully and slowly; if any substance remain, it of course indicates a degree of solubility. F. 168.

18. A solution saturated when cold, may be often obtained much more speedily by the aid of heat, as by boiling the substance with water, leaving it to cool, and afterwards filtering it, when a saturated solution will be at once obtained. If the solution while cooling deposits any portion of the solid, it

Method of ob-
taining a cold
saturated so-
lution.

proves the saturation, if it does not, there is reason to doubt it, and heat with more of the solid substance in powder should again be applied. The solution may also be tested while hot by dipping into it a glass rod, and thus transferring a drop to a cold glass plate, if crystals or solid substance appear in a few moments, the solution will be saturated when cold. Sometimes this effect will not take place until the drop is stirred. F.

Evaporation.

19. To recover a salt from its solution, if its solubility does not vary with the temperature of the solvent, as in the instance of common salt, it is necessary to expel a portion of the fluid by heat. This constitutes the process of *evaporation*.*

The figure influenced by rapidity of evaporation.

20. The regularity of the figure (12) obtained will be influenced by the rapidity of the evaporation; if the process be slowly conducted, the particles unite with great regularity; if hurried, the crystals are irregular and confused. In common cases the evaporation may be continued till a pellicle forms upon the surface of the solution, which indicates that the attraction of the saline particles for each other, is becoming superior to their attraction for the water. The formation therefore, of a superficial pellicle is the common criterion of the fitness of a solution for crystallization; but where the object is to obtain very regular and very large crystals, the evaporation must be much slower, and carried to much less extent; even spontaneous evaporation, or that which takes place at common temperatures, must be resorted to.

Time for stopping artificial evaporation.

Crystals formed by fusion.

21. There are certain bodies which may be dissolved or liquified by heat, and during slow cooling, may be made to crystallize. This is the case with many of the metals, with spermaceti, sulphur, &c.† Some other substances, when heated, readily assume the state of vapour or are *sublimed*, and during condensation, present regular crystalline forms; such as iodine, benzoic acid, camphor, &c.: and crystals of snow are produced by the condensation and cooling of aqueous vapour.

Crystallization of substances whose composition is feeble.

22. Some substances are so easily decomposed by heat, and at the same time retain water with such avidity, that it is impossi-

* *Apparatus for solution and evaporation.*—The vessels required for the purposes of solution and evaporation should resist the action of heat, acids, alkalies, all aqueous solutions, and for convenience should as often as possible be transparent. Solutions may be made in glasses of the forms represented by (figures 22 pl. ix.): they should be from a gill to two or three pints in capacity. For evaporation, lipped earthen ware basins, (figs. 7, 8, 9, pl. ix.) and a dish or two made of pure silver, and a platinum capsule are sometimes necessary. The latter should have a projecting tongue of metal to serve as a handle by which they may be held with a pair of pincers. Very useful glass dishes and capsules may be made out of old retorts, receivers and flasks. Solutions are often made in Florence and other flasks, (pl. 1, fig. 31.); they should be of pretty uniform thickness, but not so thick as to be liable to rupture by heat.

† The crystallization of the metals succeeds best with large quantities. The metal usually employed to illustrate this is bismuth; it should be fused in an iron ladle, and then placed on a sand bath to cool very gradually. When a solid crust has formed, holes should be broken through it at two opposite parts near the edge, with a hot iron rod, and the fluid metal beneath rapidly poured out. When that which remains in the ladle is examined, it will be found crystallized in the interior. A crucible may be used in place of an iron ladle for metals, a glass flask or an evaporating basin for sulphur, spermaceti, &c. When the experiment is made with sulphur, the temperature should not be raised too high, or the fluid will thicken and become adhesive. F.

ble to crystallize them by any of the above processes; in these cases crystallization may sometimes be effected by placing the solution under the exhausted receiver of an air-pump, over the surface of sulphuric acid, which, by absorbing the vapour as it rises, causes rapid evaporation without increase of temperature.

23. In the act of separating from the water in which they were dissolved, the crystals of almost all salts carry with them a quantity of water which is essential to the regularity of their form, and cannot be expelled without reducing them to shapeless masses. It is termed their *water of crystallization*.

Water of crystallization.

24. The hardness, brilliancy, and transparency of crystals, also often depend upon their containing this water, which sometimes exists in them in large quantities. Thus, sulphate of soda, in the state of crystals, contains more than half its weight. Sulphate of lime, in its crystallized form, contains about 20 per cent. of water, which it loses at a red heat, and the crystals crumble down into the white powder called Plaster of Paris. Some salts part with it by simple exposure to dry air, when they are said to *effloresce*; but there are other salts which *deliquesce*, or attract water from the atmosphere. Those crystals which effloresce by exposure to air, may often be conveniently preserved, by slightly oiling their surfaces. The best method is to soak the crystals in oil for a few hours, and then to wipe them and put them up in bottles.

Efflorescence and deliquescence.

25. Salts, in crystallizing, frequently inclose mechanically within their texture particles of water, by the expansion of which, when heated, the salt is burst with a crackling noise into smaller fragments. This phenomenon is called *decrepitation*.

Decrepitation.

26. Those crystals in which the water of crystallization is so abundant, as to liquefy them on the application of heat, are sometimes said to undergo the *watery fusion*.

Watery fusion.

27. Some salts, in consequence probably of their strong attraction for the water that retains them in solution, cannot be brought to crystallize in the ordinary way. In such cases, crystallization may be effected by the addition of substances having a strong affinity for water, by which its attraction for the dissolved matters is weakened; thus alcohol, added to certain aqueous saline solutions, (as solution of nitre) produces a separation of crystals, but they are generally small and indistinct.

28. When two salts of different solubilities are present in the same solution, they often may be separated by crystallization, that which is least soluble constituting the earlier crop of crystals.

29. Crystallization is accelerated by introducing into the solution a nucleus, or solid body, upon which the process begins; and manufacturers often avail themselves of this circumstance. Thus we see sugar-candy crystallized upon strings, and verdigris upon sticks. There are cases in which it is particularly advantageous to put a few crystals of the dissolved salt into the solution, which soon cause a crop of fresh crystals. In some

Crystallization promoted by a nucleus.

instances, if there be two salts in solution, that will most readily separate of which the crystals have been introduced.

Method of obtaining perfect crystals,

30. By placing a crystal of the same nature in a saturated solution of a salt; and turning it daily, so that the different sides shall be successively exposed to the liquid, very large and perfect crystals may be obtained. This fact was first noticed by M. Le Blanc of Paris.

Dr Wollaston's method.

31. Dr Wollaston has made known a method of gradually converting several small crystals into one large one, which has been thus described by Mr Faraday. If a small quantity of sulphate of nickel in solution, with a slight excess of acid, be evaporated in a watch glass, it will probably, on cooling yield a crop of numerous small crystals; but if set aside for a few weeks in a place subject to the changes of atmospheric temperature, its appearance will gradually alter, the small crystals disappearing, the larger increasing, until ultimately only one or a few large ones are left. This effect depends on the greater extent of surface exposed by the small crystals, as compared to their mass, than by the larger crystals; so that when any increase of solvent power in the surrounding fluid is occasioned by a slight increase of heat in the atmosphere, the small crystals dissolve to a greater extent than the others; but upon the decrease of temperature, the deposition is equal upon all. In this manner the small ones are gradually dissolved, and the large ones become larger. Thus sometimes a separation from impurities, a perfection of form, or a crystal of magnitude is obtained, which cannot be had by other means. The same effect may often be observed in solutions confined in glass bottles, as in oxalic acid, nitrate of mercury, acetate of lead, &c. the small crystals which were formed when the solutions were first made being gradually converted into others of considerable magnitude.

Circumstances affecting forms.

32. The influence exerted over one substance by the presence of another, often materially affects the appearance of crystals. Nitre, when crystallizing from solutions containing much common salt, is frequently rough upon its surface, or constituted of a number of crystals, forming a friable, instead of a compact mass. Common salt, when crystallized from a solution containing urea, assumes an octoedral form. The appearances of several salts are altered when crystallized in animal or vegetable infusions.

33. Sometimes crystallization is *not* effectual for the separation of salts. When the sulphates of iron and copper are in solution together, crystals will be obtained resembling those of sulphate of iron, but with very variable proportions of sulphate of copper in them, the latter salt being at times present in great quantity; on other occasions triple salts are formed, as frequently occurs with nickel. F. p. 254.

34. The pressure of the atmosphere has been said to have considerable influence on crystallization.

Make a concentrated solution of sulphate of soda (Glauber's salt,) in the proportion of about three parts of the salt in crystals, to two of water, boil it briskly in a matrass and cork it tightly while hot. This solution will remain fluid when cold; but will generally crystallize when the cork is withdrawn; should it not, the introduction of a piece of the same salt will effect it. Exp.

This phenomenon has not been satisfactorily explained. That it is not dependant on atmospheric pressure is proved by cooling the solution in an open vessel, the surface being covered only with a thin film of oil.*

35. The presence of light also influences the process of crystallization. Thus we see the crystals collected in camphor bottles in druggists' windows always most copious upon the surface exposed to light; and if we place a solution of nitre in a room which has the light admitted only through a small hole in the window shutter, crystals will form most abundantly upon the side of the basin most exposed to the aperture through which the light enters, and often the whole mass of crystals will turn towards it. Light influences crystallization.

Many saline solutions form arborescent crystalline pellicles when left to spontaneous evaporation, which slowly travel up the sides of the basin, and gradually proceed down upon the outside: this process also always begins on the side nearest the light, and is often confined to it. Acetate of lime, exhibits this appearance in a very beautiful manner. *Aikin's Dict.*
Art. LIGHT.

36. We may now proceed to examine the structure of crystallized bodies, upon which the *Theories of Crystallization* are founded. This inquiry exposes a connecting link between the chemical and mechanical properties of bodies. Structure of crystallized bodies.

It is commonly observed, that crystallized bodies affect one form in preference to others. Fluor spar crystallizes in cubes: so does common salt. Nitre assumes the form of a six-sided prism, and alum that of an octoedron. These forms are liable to vary. Fluor spar and salt crystallize sometimes in the form of octoedra; and there are so many forms of carbonate of lime, that it is difficult to select that which most commonly occurs. Assume one form rather than another.

Romé de Lisle referred these variations of form to certain truncations of an invariable primitive nucleus; and Gahn afterwards observed, that when a piece of calcareous spar was carefully broken, all its particles were of a rhomboidal figure. This induced Bergman to suspect the existence of a primitive nucleus in all crystallized bodies. (*Physical and Chemical Essays*, Vol. II. p. 1.) When Haüy entered the field of inquiry, he not only corroborated the opinions of Bergman, and submitted former hypotheses to experimental proof, but traced with much success the laws of crystallization and pointed out the modes of transition from primitive to secondary figures. *Traité de Minéralogie*, Paris, 1801. All varieties of crystals of the same substance have similar nuclei.

* See papers on this subject by Dr. Ure, Quart. Jour. Vol. x. p. 6, and Guy Lussac, An. de Chem. Vol. 87.

Crystals cannot be split smoothly but in certain directions.

Haüy's primitive forms.

Pl. 1.

Integral molecule.

37. Every crystal may be divided by means of proper instruments; and, if split in certain directions, presents plane and smooth surfaces. If split in other directions, the fracture is rugged, is the mere effect of violence, and is not guided by the natural joining of the crystal. This fact has been long known to jewellers and lapidaries; and an accidental observation of it proved to the Abbé Haüy, the key of the whole theory of crystallization. By the skilful division of a six-sided prism of calcareous spar, he reduced it to a rhomb, precisely resembling that which is known under the name of Iceland spar. Other forms of calcareous spar were subjected to the same operation; and, however different at the outset, finally agreed in yielding, as the last product, a rhomboidal solid. It was discovered also by Haüy, that if we take a crystal of another kind (the cubic fluor spar, Derbyshire spar for instance,) the nucleus, obtained by its mechanical division, will have a different figure, viz. an octoedron. Other crystallized bodies produce still different forms; which are not, however, very numerous. Those which have hitherto been discovered, are reducible to six; the parallelopiped, fig. 1, which includes the cube, the rhomb, and all the solids which are terminated by six faces, parallel two and two; the tetraedron, fig. 2; the octoedron, fig. 3; the regular hexaedra prism, fig. 4; the dodecaedron with equal and similar rhomboidal planes, fig. 5; and the dodecaedron with triangular planes, fig. 6.

38. The solid of the primitive form, or nucleus of a crystal obtained by mechanical division, may be subdivided in a direction parallel to its different faces. All the sections thus produced being similar, the resulting solids are precisely similar in shape to the nucleus, and differ from it only in size, which continues to decrease as the division is carried farther. To this division, however, there must be a limit, beyond which we should come to particles so small, that they could no longer be divided. At this term therefore, we must stop: and to these last particles, the result of an analysis of the primitive nucleus, and similar to it in shape, Haüy has given the name of the *integrant molecule*. If the division of the nucleus can be carried on in other directions than parallel to its faces, the integral molecule may then have a figure different from that of the nucleus. The forms, however, of the integrant molecule, which have hitherto been discovered, are only three; the tetraedron, fig. 2, the simplest of pyramids; the triangular prism, fig. 7, the simplest of prisms; and the parallelopiped, including the cube and rhomboid, the simplest of solids which have their faces parallel two and two.* With respect to octoedral crystals there is a difficulty, whether the octoedron, or tetraedron

* The instruments used for measuring the angles at which the planes of crystals meet, or incline to each other, are called *goniometers*. For the description of these and the method of using them, see Cleaveland's Mineralogy, chap. 2d. (edit. 1822.) Brooke's Crystallography, p. 25.

is to be adopted as the primitive form; and, whichever be chosen, since neither of them can fill space without leaving vacuities, it is not easy to conceive any arrangement, by which the particles will remain at rest. To obviate this difficulty, Dr Wollaston has suggested, that, in such instances, the elementary particles may be perfect spheres; and, by the due application of spheres to each other, he has shewn, that a variety of crystalline forms may be produced;* viz. the octoedron, the tetraedron, and the acute rhomboid. If other particles having the same relative arrangement, be supposed to have the shape of oblate spheroids, the regular rhomboid will be the resulting figure; and if the spheroids be oblong instead of oblate, they will generate prisms of three or six sides. The cube, also, Dr Wollaston has shown, may be explained by the aggregation of spheroidical particles.

Wollaston's theory.

39. A method of developing the structure of crystals, by a new process which appears greatly superior to that of mechanical division, has been described by Mr Daniell.† It consists in exposing any moderately soluble salt to the slow and regulated action of a solvent. A shapeless mass of alum, for instance, weighing about 1500 grains, being immersed in 15 ounce-measures of water and set by, in a quiet place, for a period of three or four weeks, will be found to have been more dissolved toward the upper than the lower part, and to have assumed a pyramidal form. On further examination, the lower end of the mass will present the form of octoedrons and sections of octoedrons, in high relief and of various dimensions. They will be most distinct at its lower extremity, becoming less so as they ascend, fig. 9. Bodies that are very soluble, in place of being immersed in water, should be put into a solution of the same substance, which having been saturated, has afterwards been slightly diluted to occasion a solvent action. Substances not soluble in water but soluble in acids, without effervescence, may be successfully examined in the same manner. This new process of dissection admits of extensive application. Borax, in the course of six weeks, exhibits eight sided prisms with various terminations; and other salts may be made to unfold their external structure by the slow agency of water, fig. 8. Carbonate of lime, carbonate of strontia, and carbonate of baryta, give also distinct results, when acted upon by weak acids; and even amorphous masses of those metals, which have a tendency to assume a crystalline form, such as bismuth, antimony, and nickel, when exposed to very dilute nitric acid, presented at the end of a few days distinct crystalline forms. Large crystals of sulphuret of antimony Mr Faraday has also found, admirably illustrate Mr Daniell's mode of displaying crystalline texture. When such a crystal is introduced into a portion of fused sulphuret, it begins to melt down, but not uniformly, for crystals are left more than half an inch long projecting from it.‡

Mr Daniell's experiments.

Pl. 1.

* Phil. Trans. 1813, p. 51.

† Jour. of Science and the Arts, i. 24.

Ibid. xi. 202.

The results of these experiments when minutely traced and investigated, afford strong confirmation to the theory, that the spheroidal is the true form of the ultimate particles of crystallized bodies. H. 1. 35, 37.

Connexion of crystallization with chemistry.

40. In connexion with chemistry, the theory of crystallization opens a new avenue to the science, and frequently enables us to ascertain directly, that, which, independent of such aids, could only be arrived at by an indirect and circuitous route. We frequently read the chemical nature of substances, in their mechanical forms. In the arts, the process of crystallization is turned to very valuable account, in the separation and purification of a variety of substances.

SECTION II. *Heterogeneous Attraction or Affinity.*

Chemical attraction or affinity.

41. We have hitherto considered attraction as disposing the particles of bodies to adhere so as to form masses or aggregates; and in many instances, to arrange themselves according to peculiar laws, and to assume regular geometrical figures.—We are now to regard this power as operating upon dissimilar particles; as presiding over the composition of bodies; and as producing their chemical varieties. This is **CHEMICAL ATTRACTION, OR AFFINITY.**

Distinguished from Cohesive Attraction.

Result of this Attraction.

42. Chemical affinity, like the cohesive attraction, is effective only at insensible distances; but it is distinguished from the latter force, in being exerted between the particles or atoms of bodies of *different kinds*. The result of its action is not a mere aggregate, having the same properties as the separate parts, and differing only by its greater quantity or mass, but a new compound, in which the properties of the components have either entirely or partly disappeared, and in which new qualities are also apparent. Thus, a piece of marble is an aggregate of smaller portions of marble attached to one another by cohesion, and the parts so attached are the integrant particles; each of which, however minute, is as perfect marble as the mass itself. But the integrant particles consist of two substances, lime and carbonic acid, which are different from one another as well as from marble, and are united by chemical attraction. The integrant particles of a body are therefore aggregated together by cohesion; the component parts are united by affinity.

Instances.

43. The most simple instance of the exercise of chemical attraction is afforded by the mixture of two substances with one another. Water and sulphuric acid, or water and alcohol combine readily. So when potassa is added to sulphuric acid chemical affinity is exerted, and they combine together. If the two last substances are examined before being presented to each other, each will be found to be distinguished by peculiar properties. The potassa will convert the blue colour of vegetable

infusions* to green, the acid will turn them red. But if we gradually add the potassa to the acid, we shall obtain a liquid which will have neither the properties of the potassa or of the acid; and which will no longer change the colour of the vegetable infusion, and the taste of which will have been converted into a bitter one.

44. In cases of this kind where chemical combination takes place, and the qualities of the component parts of a compound are no longer to be detected in it; the bodies combined are said to *neutralize* each other. Neutralization,

45. Neutralization is to be distinguished from saturation, (15) by which we express those weaker combinations where there is no remarkable alteration of qualities, as in cases of *solution*.—Water, for example, will dissolve successive portions of common salt, or sugar, until at length it refuses to take up more; or is *saturated*; the solution retaining the saline or sweet taste and some other qualities of the salt or sugar. The only physical quality that is changed being that of cohesion. distinguished from Saturation.

46. Neutralizations are best effected with the assistance of heat, especially if a carbonate be used, or if precipitation occur during the operation. The carbonic acid in the first case is dissipated, and in the latter the combination is more rapidly and perfectly effected. Evaporating basins (pl. ix. figs. 8, 9,) are highly useful for these purposes, their contents being easily stirred, and the rod used for that purpose also applied to moisten the test paper when required. The solution to be neutralized should not be very strong, and the substance added should be diluted upon approaching the point of neutralization, if it be accurately required. F. 274. Neutralization, how effected.

47. In many cases, the properties of the compounds resulting from chemical affinity differ essentially from those of their component parts, and a series of new bodies, possessed of distinct and peculiar characters, is produced. The compound may have distinct properties.

Thus when two volumes of nitric oxide gas are mixed with one of oxygen, Exp. 1.
an orange-coloured gas results, very sour, and soluble in water, whereas, the gases before mixture were colourless, tasteless, and insoluble in water.

If into a glass vessel, exhausted of air, be introduced some sulphur, and copper filings, and heat applied so as to melt the former, it will presently combine with the latter. Exp. 2.

* An infusion of purple cabbage affords an economical and convenient liquid for this and similar purposes. For its preparation, one or more red cabbages should be cut into strips, and boiling water poured upon the pieces, a little dilute sulphuric acid is to be added, and the whole well stirred: it is then to be covered and kept hot as long as possible, or if convenient, should be heated nearly to boiling for an hour or two in a copper or earthen vessel. The quantity of water to be added at first should be sufficient to cover the cabbage, and the sulphuric acid should be in the proportion of about half an ounce of strong oil of vitriol by measure to each good sized plant. This being done the fluid should be separated and drained off, and as much more hot water poured on as will cover the solid residue, adding a very little sulphuric acid. The whole is to be closed up, and suffered to stand until cooled, and then the liquid poured off and added to the former infusion. The *infusion* is to be evaporated to one half or one third its first bulk, poured into a jar, allowed to settle, and the clear red fluid decanted and preserved in bottles. This solution will keep a year. When required for use, the acid of a small portion of it should be neutralized by caustic potassa or soda, (not by ammonia) when it will assume an intensely deep blue colour, and will in most cases, require dilution with twelve or fourteen parts of water. *Faraday.*

Exp. 3.

If we mix a quantity of iron filings and sulphur, and melt them in a crucible, we obtain a brittle mass which has properties different from those of either of its constituent parts.

Results.

We observe as the results of this attraction between these substances, 1, that the substances produced have not the intermediate properties of their elements but that they present new characters; 2, that in the second experiment much heat and light are evolved during the mutual action; 3, that the substances will unite in certain proportions only.

Solid products.

48. In liquids and gases, similar changes of properties may be exhibited, and, in many cases, a change of form or state results. Thus the combination of æriform bodies produces a solid.

Pl. 3.

Exp.

Into a retort (fig. 53, *a*.) introduce a small quantity of liquid ammonia (volatile alkali,) and into another a little muriatic acid; insert the beaks of the retorts into the extremities of a glass cylinder. The gases arising from the muriatic acid and ammonia, pass into the cylinder and unite to form a new solid compound, muriate of ammonia (sal ammoniac.)

Exp.

If to a concentrated solution of muriate of lime, sulphuric acid or a saturated solution of carbonate of potassa be gradually added, a white solid will result.

Caseous.

49. In other cases the solids are converted into æriform matter, of which the combustion of gunpowder is a familiar instance.—Gases also, form a liquid; as when olefiant gas is mixed with chlorine.

When certain liquids are presented to each other, gases are the result, as when to two parts of alcohol we add one part of nitric acid, an effervescence ensues, and æriform matter is copiously evolved.

Liquid.

Exp.

Solids also produce liquids.

Rub together in a mortar a few crystals of Glauber's salt with nitrate of ammonia, the two solids will become fluid.

Such operations are not confined to art. Nature presents them on an extended scale; and in connexion with the functions of life, renders them subservient to the most exalted purposes.

50. The new chemical powers that bodies thus acquire in consequence of combination, are often extremely remarkable, and can only be learned by *experiment*. It frequently happens that inert bodies produce inert compounds, and that active substances remain active when combined; but the reverse often occurs: thus oxygen, sulphur, and water, in themselves tasteless and comparatively inert, produce sulphuric acid when chemically combined; and potassa, which is a powerful caustic, when combined with sulphuric acid, forms a *salt** possessing little activity.

Other changes produced by Chemical action.
Exp.

51. The colours of bodies are altered by chemical action.

Into a weak solution of nitrate of copper, drop liquid ammonia, a rich blue colour will be produced. Add gradually, on the end of a glass rod, a little sulphuric acid, the liquid will become colourless.

* The term *salt* is employed in chemistry to denote a compound of acid matter with an alkali, earth, or metallic oxide, and is therefore not confined to those substances called salts in ordinary discourse.

To an infusion of purple cabbage add a few drops of an acid, the colour will be changed to red.—The addition of liquid potassa, in quantity just sufficient to neutralize the acid, will restore the original colour. Exp.

The addition of potassa alone, produces a green colour. Exp.

Into a small jar of chlorine gas, confined by water, introduce a piece of litmus paper, the colour will be wholly destroyed. Exp.

When sulphate of copper (blue vitriol,) and acetate of lead (sugar of lead) are rubbed together in a mortar; the new compound has a green colour. Exp.

Calomel and potassa, both colourless, when rubbed in a mortar form a black compound. Exp.

52. The specific gravity of bodies is altered by chemical action. Two bodies rarely occupy the same space after combination which they did separately. In general their bulk is diminished, so that the specific gravity of the new body is greater than the mean of its components. Thus a mixture of 100 equal measures of water and an equal quantity of sulphuric acid does not occupy the space of 200 measures, but considerably less. A similar contraction frequently attends the combination of solids. Gases often experience a remarkable condensation when they unite. The elements of olefiant gas, for instance, would expand to four times the bulk of that compound, if they were suddenly to become free, and assume the æriform state. But there are exceptions. The reverse happens in some metallic compounds; and there are examples of combination between gases without any change in bulk. Change of specific gravity,

53. A change of temperature generally accompanies chemical action. Caloric is evolved either when there is a diminution in the bulk of the combining substances without a change of form, or when a gas is condensed into a liquid, or when a liquid becomes solid, (34) as when water is poured upon quicklime. and of temperature.

When equal parts of sulphuric acid and water are mixed, the temperature is so much increased that if the mixture be made in a phial about which tow is wrapped containing a small piece of phosphorus, the phosphorus will be inflamed. Exp.

54. Ignition is a frequent attendant upon chemical action, Ignition.
(47.)

Mix, cautiously, a small quantity of sugar with about half its weight of the salt called chlorate of potassa. drop upon the mixture, from the extremity of a glass rod, a little sulphuric acid, it will be inflamed. Exp.

55. As chemical action takes place among the ultimate or constituent elements of bodies, it must obviously be opposed by the cohesion of their particles, and chemical attraction is often prevented by mechanical aggregation. Chemical action promoted by mechanical division,

Introduce a piece of the metal antimony into a jar of chlorine gas, it will be only slowly and superficially acted upon; but if the mechanical aggregation be previously diminished, by reducing the metal to powder, it in that state rapidly unites with the gas, and burns the instant that it is introduced. Exp.

The influence of mechanical division in promoting the action of chemical affinity, and in favouring solution, will be obvious, if into a vessel containing dilute muriatic acid we drop a lump of marble; and into another vessel containing the same acid we pour an equal weight of marble reduced to powder.

by Caloric, 56. The chemical energies of bodies, are increased by heat.
 Exp. To four ounce-measures of water, at the temperature of the atmosphere, add three ounces of sulphate of soda in powder, only part of the salt will be dissolved, even after being agitated some time. Apply heat, and the whole of the salt will disappear.

To this law, however, there are several exceptions; for many salts are equally, or nearly equally, soluble in cold as in hot water; as will be seen hereafter.

The effects of heat are sometimes only referable to the diminution of adhesion by expansion, or liquefaction; but in other cases they are peculiar and complicated, and probably concerned in modifying the electrical energies of the acting substances.

and by Mechanical agitation. 57. Mechanical agitation, also favours the chemical action of bodies.

Exp. Into a wine glass full of water, tinged blue with the infusion of cabbage, let fall a small lump of solid tartaric acid. The acid, if left at rest, even during some hours, will only change to red that portion of the infusion, which is in immediate contact with it. Stir the liquid, and the whole will immediately become red.

Force of affinity varies. 58. An important law of affinity which is the basis of almost all chemical theory, is that one body has not the same force of affinity towards a number of others, but attracts them unequally; or different bodies are possessed of different attractive powers, and if several be brought together, those which have the strongest mutual affinities enter first into union.

Exp. Thus, if nitric acid be poured upon a mixture of lime and magnesia, it dissolves the former in preference to the latter earth.

Some bodies have no affinity for each other. 59. Some bodies evince no affinity for each other.

Exp. Oil and water, or powdered chalk and water, may be agitated together, but they will not combine. On allowing the vessels containing them to remain at rest, the oil or water rises to the surface, and the chalk falls to the bottom.

Union promoted by a third body. 60. The intervention of a third body will sometimes promote the union of two other bodies which have no affinity for each other.

Exp. Thus oil and water unite immediately on adding an alkali, as caustic potassa. The fact indeed, admits of being explained by the supposition, that the oil and alkali form, in the first instance, a compound which is soluble in water. (H.)

or destroyed. 61. It very frequently happens, on the contrary, that the tendency of two bodies to unite, or remain in combination together, is weakened or destroyed by the addition of a third. Thus alcohol unites with water in such a manner as to separate most salts from it.

Exp. A striking instance of this is seen in a saturated or strong solution of nitre in water. If to this there be added an equal measure of alcohol, the greater part of the nitre instantly falls down.

Exp. Or, if to a solution of camphor in alcohol, water be added, the water will unite with the alcohol and the camphor will be separated.

Exp. Oil has an affinity for the volatile alkali, ammonia, and will unite with it, forming a soapy substance called a liniment. But the ammonia has a still greater attraction for sulphuric acid; and hence if the acid be added to the liniment, the alkali will quit the oil, and unite by preference with the acid.

Affinity how inferred. 62. The affinity existing between any two bodies, is inferred from their entering into chemical combination and that this has

happened, a change of properties may be considered as a sufficient proof, even though the change may not be very obvious and may require accurate examination to be perceived at all.—H. 1. 41.

63. The knowledge of the affinities which bodies have for each other, enables us to separate them when united, or to perform the process of *decomposition*. Thus, if into a solution of nitrate of silver (lunar caustic) we place a piece of polished copper, it will soon be covered with metallic silver and the solution will have been *decomposed*, and the silver *precipitated*. Simple or
elective At-
traction.

Exp.

64. From a great number of facts of this nature, it is clearly ascertained, not as a probable hypothesis, but as a simple matter of fact, that some bodies have a stronger tendency to unite than others; and that the union of any substance with another will exclude, or separate, a third substance which might have been previously united with one of them; excepting in those cases wherein the new compound has a tendency to unite with that third substance, and form a triple compound. This preference of uniting, which a given substance is found to exhibit with regard to other bodies, Bergmann called *elective attraction*.—(U. 187.)

65. Upon this principle, tables of attraction have been constructed, the substance whose affinities are to be represented being placed at the head of a column, and the bodies with which it combines beneath it, in the order of their respective attractions (see *Brande's History of Chemistry*, p. 78;) thus the affinity of sulphuric acid for several substances (or bases) would be shown as follows: Tables of
Attraction.

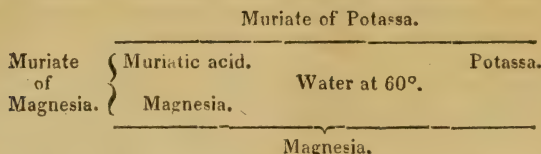
SULPHURIC ACID.

Baryta.
Strontia.
Potassa.
Soda.
Lime.
Ammonia.

From this table it would appear that baryta separates sulphuric acid from its compounds with all the inferior substances, and that ammonia is separated by all that are above it. There are, however, many circumstances which interfere with the usefulness and accuracy of such tables. The relative forces of chemical attraction cannot always be determined by observing the order in which substances separate each other when in combination; and in some cases there are anomalies in the mutual agencies of bodies which wholly subvert the usual order of arrangement. One of these has been pointed out by Mr R. Phillips,—(*Quarterly Journal*, Vol. i. p. 80.)

66. Simple decomposition may be expressed also by another form, contrived by Bergmann. Thus, the following scheme Bergmann's
form.

illustrates the decomposition of muriate of magnesia by potassa :



The original compound (muriate of magnesia) is placed on the outside and to the left of the vertical bracket. The included space contains the original principles of the compound, and also the body which is added to produce decomposition. Above and below the horizontal lines are placed the results of their action. The point of the lower horizontal line being turned downwards, denotes that the magnesia falls down or is precipitated ; and the upper line, being perfectly straight, shows, that the muriate of potassa remains in solution. If both the bodies had remained in solution, they would both have been placed above the upper line ; or, if both had been precipitated, beneath the lower one. If either one or both had escaped in a volatile form, this would have been expressed by placing the volatilized substance above the diagram, and turning upwards the middle of the upper horizontal line. But since decompositions vary under different circumstances, it is necessary to denote, by the proper addition to the scheme, that the bodies are dissolved in water of the temperature of 60°. H. 1. 54.

67. Decomposition is effected under a variety of circumstances, and by many methods ; but it is commonly described by chemists as SIMPLE and COMPLEX or SINGLE and DOUBLE.

Single decomposition.

68. In cases of simple attraction or affinity, one body separates another from its combination with a third. Thus when potassa is added to a solution of sulphate of zinc (composed of sulphuric acid and oxide of zinc,) the oxide of zinc is separated, and sulphate of potassa is produced ; and in the experiments (61) the substances added manifest, as it were, a choice for one of two others uniting with it by preference and to the exclusion of the other. Many of the decompositions that occur in chemistry are instances of single elective affinity.

Double decomposition.

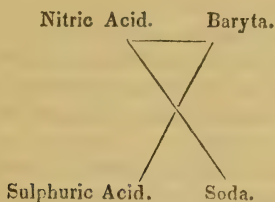
69. In cases of double decomposition, two new compounds are produced ; as when a solution of nitrate of baryta, is mixed with a solution of sulphate of soda, the results are a precipitate of sulphate of baryta, and a solution of nitrate of soda.

Exp.

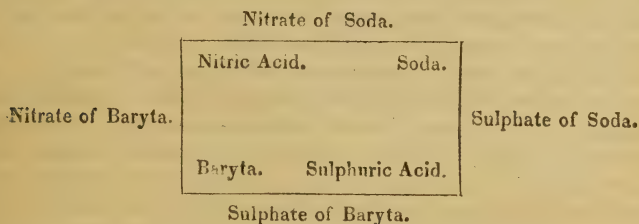
In a watery solution of sulphate of zinc (white vitriol) immerse a thin sheet of lead ; the lead will remain unaltered, as also will the sulphate of zinc, because zinc attracts sulphuric acid more strongly than lead. But let a solution of acetate of lead be mixed with one of sulphate of zinc ; the lead will then go over to the sulphuric acid, while the zinc passes to the acetic. The sulphate of lead being insoluble, will fall down in the state of a white powder ; but the acetate of zinc will remain in solution. (H.)

70. These cases of double decomposition are sometimes conveniently illustrated by diagrams, which may either be

constructed so as merely to show the result of the change, or where required they may also exhibit the composition of the acting bodies. In the case just alluded to (69) the substances before mixture are shown by parallel lines, and after mixture by diagonal lines.



Or a more complete view of the change is given in the following diagram, where the bodies before mixture are placed upon the outside of the perpendicular lines; their component parts are shown within them; and the new results on the outside of the horizontal lines.



71. It is obvious, from the uniform results of chemical action that affinity must be governed by certain definite laws, by which its results are determined, and upon which its uniformity depends. Attention was first called to this subject by Mr Higgins in 1789,—(*Comparative View of the Phlogistic and Antiphlogistic Theories.*) He conceived that chemical attraction only prevailed between the ultimate particles of simple elementary matter, and between compound atoms; and, in applying this idea to chemical theory, he expressed by numbers the relative forces of attraction subsisting between the different kinds of ultimate particles and atoms of matter.

Chemical affinity governed by definite laws.

Higgins' idea.

72. These views were subsequently extended and improved by Mr Dalton, and have since engaged the attention of some of the most eminent chemical philosophers; among whom we may enumerate Gay Lussac, Berzelius, Davy, Wollaston, Thomson and Brande.

Made a system or theory by Dalton.

73. In the chemical combination of bodies with each other we remark,

Laws of combination.

1st Some bodies unite in all proportions; for example, water and sulphuric acid, or water and alcohol.

2dly. Other bodies combine in all proportions, as far as a certain point, beyond which, combination no longer takes place.

Thus water will take up successive portions of common salt, until at length it becomes incapable of dissolving any more. In cases of this sort, as well as in those included under the first head, combination is weak and easily destroyed, and the qualities which belonged to the components in their separate state, continue to be apparent in the compound.

Definite proportions.

3dly. In other cases bodies unite in a few proportions only. Of these bodies some form but one combination. Thus, there is but one compound of zinc and oxygen, or of chlorine and hydrogen. Others combine in two proportions. For example, two compounds are formed by copper and oxygen, or by hydrogen and oxygen. Other bodies again unite in three, four, five or six proportions, which is the greatest number of compounds that any two substances are known to produce, excepting those which belong to the first division.

When bodies unite in a few proportions, their compounds formed, so long as they retain their characteristic properties, always consist of the same elements united together in the same proportion. Sulphuric acid, for example, is always composed of sulphur and oxygen in the ratio of 16 parts, by weight, of the former, to 24 of the latter; no other elements can form it, nor can its own elements form it in any other proportion.

So also when bodies unite in several proportions, these proportions are definite, and, in the intermediate ones, no combination ensues. Thus 6 parts by weight of charcoal combine with 8 of oxygen, or with 16, but with no intermediate quantity; 64 parts of copper combine with 8 of oxygen, or with 16, and with those proportions only.

Law of multiples.

74. Now it is remarkable, that when one body enters into combination with another, in several different proportions, the numbers indicating the greater proportions are exact simple multiples of that denoting the smallest proportion. In other words, if the smallest proportion in which B combines with A, be denoted by 10, A may combine with twice 10 of B, or with three times 10, and so on; but with no intermediate quantities. There cannot be more striking instances of this law than those above mentioned, of the compounds of copper and charcoal with oxygen; in which the oxygen of the last compound may be observed to be a multiple of that of the first by the number 2. H. 1. 43.

Table of combining proportions of Oxygen.

75. The following table exhibits the proportions by weight in which oxygen combines with several other bodies (or bases,) in which it will be observed that the numbers denoting the oxygen attached to the same body bear a very simple ratio to each other.

Table.

| | | | | | |
|---------------------------------|----------------|----------|---|--------|----|
| Water | is composed of | Hydrogen | 1 | Oxygen | 8 |
| Deutoxide of Hydrogen | " | " | 1 | " | 16 |
| Carbonic oxide | " | Carbon | 6 | " | 8 |
| Carbonic acid | " | " | 6 | " | 16 |

| | | | | | |
|--------------------|----------------|----------|----|--------|----|
| Hypsulphurous acid | is composed of | Sulphur | 16 | Oxygen | 8 |
| Sulphurous acid | “ | “ | 16 | “ | 16 |
| Sulphuric acid | “ | “ | 16 | “ | 24 |
| Nitrous oxide | “ | Nitrogen | 14 | “ | 3 |
| Nitric oxide | “ | “ | 14 | “ | 16 |
| Hypnitrous acid | “ | “ | 14 | “ | 24 |
| Nitrous acid | “ | “ | 14 | “ | 32 |
| Nitric acid | “ | “ | 14 | “ | 40 |

It is manifest from these examples, that bodies unite according to proportional numbers, and hence has arisen the use of certain terms, as *proportion*, *representative numbers*, &c. to express them.

76. Compound bodies obey the same law, and the proportions in which they combine may likewise be expressed by numbers. Thus since water is composed of 1 proportion of oxygen and 1 of hydrogen, and as the oxygen is 8 times heavier than the hydrogen, 9 will be the weight of 1 proportion of water. The proportional or representative number of sulphuric acid will be 40, because it is a compound of one proportion (or 16 by weight) of sulphur and three proportions (or 24 by weight) of oxygen. Now when these compounds unite, one proportion of the one combines with one, two, three or more proportions of the other precisely as the simple substances do. The hydrate of potassa for example, is constituted of 48 potassa and 9 of water, and its representative number will be 48+9 or 57. The sulphate of potassa is composed of 40 sulphuric acid + 48 potassa, and its number will be 40+48 or 88.

Compound bodies obey the same law.

77. The same compound body is always of the same composition; no variation in the proportion of its elements can by any possibility take place: 48 parts of potassa combine with 54 parts of nitric acid to produce 102 parts of nitre; no method of putting the substances together, as by causing an excess of the one or the other, or abstracting one from a previous state of combination, or allowing other substances to be present, can cause any change in these proportions. Nor is this confined to the numbers 48, 54 and 102, but whatever may be the quantity of these elements in combination, or of the nitre produced, the proportions will be the same.

Their composition uniform.

78. Hence the composition of a substance being once accurately ascertained, it requires no further investigation; for whenever that substance re-occurs, whatever may be its quantity, the proportion of the elements existing in it may be deduced from the former determination; and whether nitre be produced by combining together pure nitric acid and potassa, or by using nitric acid with carbonate of potassa, or precipitating a nitrate of copper by potassa, or in any other manner, still it will contain the above proportions of potassa and nitric acid: whatever its quantity, yet $\frac{48}{102}$ parts of it will be potassa, and $\frac{54}{102}$ nitric acid. It is but another form of this natural law to say that the same quantity of an element always requires the same quantity of another element to form the same resulting compound.

Their composition how deduced.

Neutraliza-
tion.

79. It has been remarked (44) that when bodies mutually disguise each others properties, they are said to *neutralize* each other: an effect especially exemplified in the union of acids and alkalies. The neutralizing power of the different alkalies is very different. Thus 10 of Fluoric acid will be neutralized by 18 of lithia, or by 32 of soda, or by 78 of baryta. Or 28 of lime will be neutralized by 28 of phosphoric acid, or by 40 of sulphuric, or 62 of arsenic acid.

If a quantity of sulphate of soda in solution be poured into a solution of nitrate of baryta, the latter being in excess, a quantity of sulphate of baryta will precipitate, and nitrate of soda will remain in solution with the excess of nitrate of baryta. So much of the nitrate of baryta will be decomposed as is sufficient to supply the necessary quantity of baryta to combine with the whole of the sulphuric acid in the sulphate of soda, and to form sulphate of baryta with it, but the point now to be observed is, that the quantity of nitric acid which leaves the baryta, will be exactly that required to combine with the soda separated from the sulphate of soda, to form with it the neutral salt, nitrate of soda; for the two solutions, after mixture and chemical change, will be found as neutral as before.

It is evident from this experiment, that the nitric acid is exactly equivalent in combining and saturating power with the sulphuric acid; for they have both equally neutralized the portion of soda in the solution, and what is more, they have also both equally neutralized the portion of baryta, which has changed acids during the experiment. It will be perceived too, that the baryta in the sulphate, and the whole of the soda, are similarly circumstanced with respect to each other; for they have both exactly neutralized the active portions of the two acids. The excess of nitrate of baryta undergoes no change during the experiment, and is merely considered as present to ensure the total decomposition of the sulphate of soda.

Meaning of
the term
equivalent.

80. Similar phenomena are presented by all other neutral saline bodies; the reciprocity of saturating power is found to exist as above described whenever chemical change takes place, and is therefore dependant upon no particular body, but belongs to all. Hence a correct notion may be formed of the meaning of the term *equivalent* as applied to bodies acting chemically. The quantities of substances, which, by combining together saturate each other, are *equivalent* in their power of combination; thus 40 parts of sulphuric acid are equivalent to the saturation of 78 parts of baryta. The quantities of two or more substances which combine with and saturate an equal quantity of the same substance, are *equivalent* to each other in their saturating power; thus 40 parts of sulphuric acid and 54 parts of nitric acid are equivalents, for both are competent to combine with and neutralize 32 parts of soda or 78 parts of baryta: and the latter are equivalents for the same reason. Also the quantities of compound bodies which mutually act upon each other

are *equivalents*, because the same proportional quantities are always necessary and always sufficient.

The term *chemical equivalent* may therefore be used to imply that proportion of a body which is necessary to act upon another body, the circumstances of chemical affinity being such as to permit action to take place; and it has been found that the proportions are the same for one body, whatever other body it be compared with. So that if a particular number be arbitrarily taken to represent the quantity of any one substance competent to enter into combination, and be called its *equivalent*, then all the equivalents of other substances may be set down in numbers, those numbers being in the same proportion to the first number, that the combining quantities they represent are, to the combining quantity of substances to which that first number belongs. Thus in the change between nitrate of baryta and sulphate of soda, (79), suppose the number 40 to be assumed as the equivalent number of the sulphuric acid present, then 32 will be the equivalent of the soda, for so much is combined with the 40 of sulphuric acid; and 54 will be the equivalent of the nitric acid, for so much will combine with the 32 of soda, and 78 will be the equivalent of the baryta; 118 will be the equivalent of the sulphate of soda, 132 of the nitrate of baryta, and 86 of the nitrate of soda. F. 554.

81. The determination of these equivalents, or proportional numbers, is purely a matter of experiment. The commencement is made by carefully analyzing a definite compound of two simple substances which possess an extensive range of affinity. No two bodies are better adapted for this purpose than oxygen and hydrogen, and that compound is selected which contains the smallest quantity of oxygen. Water is such a substance, and it is therefore regarded as a compound of one proportion of oxygen to one proportion of hydrogen. But analysis proves that it is a compound of 8 parts by weight of the former to 1 of the latter, by which the relative weights of their proportions are determined, that of oxygen being eight times heavier than that of hydrogen.

Some compounds are next examined which contain the smallest proportion of oxygen or hydrogen in combination with some other substance, the quantities of each being the smallest that can unite together. Carbonic oxide with respect to carbon, and sulphuretted hydrogen with respect to sulphur, answer this description perfectly. The former consists of 8 oxygen and 6 carbon; the latter of 1 hydrogen and 16 sulphur. The proportional number of carbon is consequently 6, and of sulphur 16. The proportions of all other bodies may be determined in the same manner.

82. Since these numbers merely express the relative quantities of different substances which combine together, it is in itself immaterial what figures are employed to express them. The only essential point is, that the relation should be strictly

Determina-
tion of Equi-
valents.

Immaterial
what figures
are employed.

observed. Thus, we may make the combining proportion of hydrogen 10 if we please ; but then oxygen must be 80, carbon 60, and sulphur 160. T. 127.

Dr Wollaston's Scale.

83. These equivalent numbers, when once well ascertained and arranged in a tabular form, become a safe and invaluable source of information to the chemist. By adapting a table of this sort to a moveable scale, on the principle of Gunter's sliding rule, Dr Wollaston has constructed a *logometric scale of chemical equivalents*, which is capable of solving with great facility many problems of chemistry.*

Atomic Theory.

84. To account for the laws observed with regard to these definite combinations Mr Dalton has proposed what may be termed the *Atomic Theory of the chemical constitution of bodies*.

Though we appear when we effect the chemical union of bodies, to operate on *masses*, yet it is consistent with the most rational view of the constitution of bodies to believe, that it is only between their *ultimate particles*, or atoms, that combination takes place. By the term *atoms*, it has been already stated, we are to understand the smallest parts of which bodies are composed. An atom therefore, must be mechanically indivisible, and of course a fraction of an atom cannot exist.—Whether the atoms of different bodies be of the same size, or of different sizes, we have no sufficient evidence.

Taking for granted that combination takes place between the atoms of bodies only, Mr Dalton has deduced, from the relative weights in which bodies unite, the relative weights of their ultimate particles or atoms. When only one combination of any two elementary bodies exists, he assumes, unless the contrary can be proved, that its elements are united atom to atom singly. Combinations of this sort he calls *binary*. But if several compounds can be obtained from the same elements, they combine, he supposes, in proportions expressed by some simple multiple of the number of atoms. The following table exhibits a view of these combinations :

| | | | | | |
|--------------|---|--------------|---|--------------|--------------|
| 1 atom of A | + | 1 atom of B | = | 1 atom of C, | binary. |
| 1 atom of A | + | 2 atoms of B | = | 1 atom of D, | ternary. |
| 2 atoms of A | + | 1 atom of B | = | 1 atom of E, | ternary. |
| 1 atom of A | + | 3 atoms of B | = | 1 atom of F, | quaternary. |
| 3 atoms of A | + | 1 atom of B | = | 1 atom of G, | quaternary.† |

Weight of atoms.

If water, for example, is composed of an atom of hydrogen and an atom of oxygen, it follows that every compound of hydrogen with an additional quantity of oxygen must contain 2, 3,

* For a description of this instrument see the appendix.

† A different classification of atoms has been proposed by Berzelius ; viz. into 1, *elementary* ; 2, *compound atoms*. The compound atoms he divides again into three different species, namely 1st, atoms formed of only two elementary substances united, or *compound atoms of the first order* : 2dly, atoms composed of more than two elementary substances ; and these, as they are only found in organic bodies, or bodies obtained by the destruction of organic matter, he calls *organic atoms* : 3dly, atoms formed by the union of two or more compound atoms ; as for example, the salts. These he calls *compound atoms of the second order*. H. 1. 44.

or more atoms of oxygen, some multiple by a whole number of the quantity of oxygen contained in water.

From this view of the composition of water it is obvious that the weight of an atom of oxygen is eight times heavier than an atom of hydrogen. The relative weight of the atoms of other substances may be determined in a similar manner. Thus an atom of carbon is six times, an atom of sulphur 16 times, and an atom of chlorine 36 times heavier than an atom of hydrogen; and this explains why they unite in proportions expressed by those numbers. What are called the proportional numbers are in fact nothing else but the relative weight of atoms.

Some chemists, even without expressly adopting the atomic theory itself, have followed Mr Dalton in the use of the terms *atom*, and *atomic weight*, in preference to *proportion*, *equivalent*, &c. All these appellations, however, have the same signification; and in using the word atom instead of the others, it should be held in mind that it merely denotes the proportions in which bodies unite.

85. An extension of the law of definite proportions, so far as respects æriiform bodies, has been proposed by Gay Lussac, namely, that they combine in proportions determinable by *volume*, the ratios being 1 *measure* of A to 1 of B, or 1 to 2, or 1 to 3, &c. Thus, 1 measure of oxygen + 1 of nitrogen unite to form nitrous gas, 1 oxygen + 2 nitrogen form nitrous oxide, 2 oxygen + 1 nitrogen form nitrous acid, &c.

Theory of
Volumes.

86. Water is composed of hydrogen and oxygen, and 1 part by weight of the former gas, unites to 8 of the latter. The specific gravity of hydrogen compared with that of oxygen, is as 1 to 16; it is obvious, therefore, that one volume of hydrogen unites to half a volume of oxygen, and that the composition of water will be represented by weight and volume thus.

| | |
|----------|---------|
| 1 | 8 |
| Hydrogen | Oxygen. |

Muriatic acid gas consists of 1 part by weight of hydrogen and 36,0 by weight of chlorine. The relative specific gravities of these gases are as 1 to 36,0. It is obvious, therefore, that they combine in equal volumes, and that muriatic acid gas may be thus represented:

| | |
|-----------|-----------|
| 1 | 36,0 |
| Hydrogen. | Chlorine. |

87. Chemists have found it convenient to refer the atomic weight of different bodies to some standard, which is assumed as the weight of an atom of some well known substance. Two

Atomic
weights refer-
red to some
body as the
unit.

bodies have been selected for this purpose, viz. oxygen and hydrogen. These bodies, as has been observed (85), unite to form water in the proportion of 8 to 1 : if we suppose therefore that this compound is formed by the combination of 1 atom of each element and if we represent the weight of the atom of oxygen by 1, we shall have for the weight of the atom of hydrogen $\frac{1}{8}$ or ,125. If on the contrary we represent the weight of the atom of hydrogen by 1, that of oxygen must be 8.

Some chemists, however, have supposed water to be formed of 2 atoms of hydrogen, united to one of oxygen, because there are two volumes of the former and one of the latter, and they consider the volumes of these gaseous bodies as representing atoms. In this case oxygen will be represented by 1, and hydrogen by $\frac{1}{16}$ or ,0625 ; or if we represent hydrogen by 1, oxygen will be 16. Dr Thompson makes oxygen 1, so that hydrogen is 8 times less than unity. or 0,25, carbon 0,75, and sulphur 2. Dr Wollaston in his scale of chemical equivalents, fixes oxygen at 10, by which hydrogen is 1,25, carbon 7,5 and so on. According to Berzelius oxygen is 100. Sir H. Davy, Dalton, Henry, Brande and others have assumed hydrogen as the unit, and have referred the weights of the atoms of other bodies to this as the standard.

Modes of as-
certaining the
composition
of bodies.

88. The proof, which establishes the nature of chemical compounds, is of two kinds, *synthesis* and *analysis*. Synthesis consists in effecting the chemical union of two or more bodies ; and analysis, in separating them from each other, and exhibiting them in a separate state. The composition of sulphate of copper (blue vitriol) is *synthetically* demonstrated by *uniting* sulphuric acid to oxide of copper. When we have a compound of two or more ingredients, which are themselves compounded also, the separation of the compounds from each other may be called the *proximate analysis* of the body ; and the farther separation of these compounds into their most simple principles, its *ultimate analysis*.

Ultimate
and

Thus the sulphuric acid of the sulphate of copper consists of sulphur and oxygen, and oxide of copper consists of copper and oxygen ; consequently we should say that the *ultimate* component parts of blue vitriol are copper, sulphur, and oxygen.

Proximate
analysis.

The proximate analysis of sulphate of potassa consists in resolving it into potassa and sulphuric acid ; and its ultimate analysis is effected by decomposing the potassa into potassium and oxygen, and the sulphuric acid into oxygen and sulphur.

When the analysis of any substance has been carried as far as possible, we arrive at its most simple principles, or *elements* ; by which expression we are to understand, not a body that is *incapable* of further decomposition, but only one which *has not yet been decomposed*. The progress of chemical science, for several centuries past, has consisted in carrying still farther the analysis of bodies, and in proving those to be compounded, which had before been considered as elementary. H. 1.

SECTION III. *Heat.*

89. No sensations are more familiar to us than those of heat and cold. They are excited by bodies applied to our organs, and at different times very different degrees of sensation are excited. The same body is capable at one time, of occasioning the feeling of intense cold ; in a short time it may convey an agreeable warmth, and by another change of circumstances, it may induce extreme heat. From this it is evident that the power of inducing these sensations does not depend upon the matter itself, which is applied to our organs ; for every shade of sensation is produced, without the qualities of that matter being permanently changed ; it is considered therefore as depending on the operation of a certain power or subtle principle, present in bodies, and which, according to its quantity, gives rise to the power of exciting different sensations.

Sensations of heat and cold.

If a piece of iron be made red hot, we conceive that a quantity of what we call *heat*, that is, of a certain subtle power, has entered into it, and that the property the iron in this state has, of affecting the organs of animals in a peculiar manner, depends on the presence of this power. When the iron is left to cool, we suppose that it parts with its excess of heat.

Heat a subtle power or principle.

90. This principle, or power, has been distinguished by various appellations, as Fire, Heat, the matter of Heat, or the Igneous fluid ; terms which are either ambiguous, or which involve some hypothesis, and which are superseded by the unexceptionable appellation of Caloric. M. 1. 183.*

Has received various names.

91. Caloric, so far as its chemical agencies are concerned, may be chiefly considered under two views—as an antagonist to the cohesive attraction of bodies—and as concurring with, and increasing elasticity. By removing the particles of any solid to a greater distance, from each other, their cohesive attraction is diminished ; and one of the principal impediments to their union with other bodies is overcome. On the other hand, caloric may be infused into bodies in such quantity, as not only to overcome cohesion, but to place their particles beyond the sphere of chemical affinity. Thus, in the class of substances, called gases, the ponderable ingredient, whether solid or liquid, is dissolved in so much caloric, that, in mechanical properties, the gases agree with the air of our atmosphere, especially in being permanently elastic. Different bodies of this class do not, in general, unite, by simple mixture. But if, of two gases, we employ either one or both in a state of great condensation, the gravitating matter of both unites, and forms a

May be considered under two views.

* Or we may define caloric as the agent to which the phenomena of heat and combustion are ascribed. U. 25.

new compound. Hydrogen and nitrogen gases, for example, may be mingled together, in the proportions adapted to form ammonia, without any production of that compound. But if hydrogen, in what has been called its nascent state, (that is, before it has acquired an atmosphere of heat and become gaseous,) be brought into contact with nitrogen gas, ammonia is then generated. (*See Ammonia.*)

In many cases, also, when two bodies are combined together, one of which is fixed, and the other becomes elastic by union with caloric, we are able, by its interposition alone, to effect their disunion. Thus carbonate of lime gives up its carbonic acid by the mere application of heat.

The state of
bodies influ-
enced by ca-
loric.

We may consider, then, all bodies in nature as subject to the action of two opposite forces, the mutual attraction of their particles on the one hand, and the repulsive power of caloric on the other; and bodies exist in the solid, liquid, or elastic state, as one or the other of these forces prevails. Water, by losing caloric, has its cohesion so much increased, that it assumes the solid form of ice; adding caloric, we diminish again its cohesion, and render it fluid; and, finally, by a still farther addition of caloric, we change it into vapour, and give it so much elasticity, that it may be rendered capable of bursting the strongest vessels. In many liquids, the tendency to elasticity is even so great, that they pass to the gaseous form by the mere removal of the weight of the atmosphere. H. 1. 78.

It expands
bodies.

92. Expansion is the most obvious and familiar effect of heat; and it takes place though in different degrees, in all forms of matter.—When a body which occasions the sensation of heat on our organs, is brought into contact with another body which has no such effect, the result of their mutual action is that the hot body contracts, and loses to a certain extent its power of communicating heat, and the other body expands, and in a degree acquires this power. D. 1. 70.

Proved by
experiment.

The expansion of solids may be made apparent by heating a rod of iron, of such a length as to be included, when cold, between two points, and the diameter of which is such, as barely to allow it to drop through an iron ring. When heated, it will have become sensibly longer; and it will be found incapable of passing through the ring.

Principle
upon which
pyrometers
are made.

93. This property of metals has been applied to the construction of an instrument for measuring temperature, called a *pyrometer*.*

Pl. 1.

* An instrument of this kind is represented by fig. 25, which will be found very convenient for showing the expansibilities of bars of different metals, at temperatures not exceeding that of boiling water. Upon a flat piece of mahogany are fixed brass studs, *g g*, on which the metallic bar, *ff*, is placed. One end of this bar bears against a lever *b* at a point very near its fulcrum; the other end of this lever, which is bent, bears against another lever *c*, the lower extremity of which is an index. Beneath this index is a graduated arc *ℓ*. When we wish to immerse the bar in hot water, or to apply heat gradually through the medium of water, the bar is passed through the brass box *a*, which has an aperture at each end. An opening is left in the board immediately under the box, to allow

94. The degree of expansion is not the same for all solids, and even differs materially in substances of the same class. Thus, the metals expand in the following order, the most expansible being placed first ; zinc, lead, tin, copper, bismuth, iron, steel, antimony, palladium, platinum. H. 1. 89.

Bodies possess different powers of expansion.

95. Solids are less expansible than liquids, and gases or æriform bodies more than liquids.

96. The expansion of liquids may be shown by the following experiment :

Expansion of liquids.

Into a glass vessel, (fig. 11) having a narrow neck, introduce some spirits of wine, and apply the heat of a lamp ; or immerse the ball of the vessel in hot water—the spirits of wine will expand and rise in the narrow neck.

Pl. 1.
Exp.

97. Liquids differ also in their relative expansibilities : ether is more expansible than spirit of wine, and spirit more than water, and water more than mercury. Those liquids are generally most expansible which boil at the lowest temperature.

Their relative expansibilities different.

This may be rendered evident by partially filling several glass tubes of equal diameters, furnished with bulbs, with the different liquids, and placing them in hot water ; as the liquids expand, they will rise to different heights in the tubes. To render this more apparent the liquids may be tinged with some colouring matter.

Exp.

The expansion of æriform bodies may be shown by filling the body of the vessel (fig. 10) with water and, keeping the finger over the orifice of the neck, inverting it in a vessel of water, the air will rise and occupy the body of the vessel ; apply the heat of a lamp, and the air will expand and cause the water to descend in the neck of the vessel.

Æriform bodies.
Exp.

If a bladder filled with air, the neck of which is closely tied, be held before a fire, it will become fully distended, and may even be burst by continuing and increasing the heat.

Exp.

98. In all pure gaseous bodies, the rate of expansion for similar increase of temperature is similar : 100 measures of air,

Rate of expansion among pure gases.

the application of a lamp. The small expansion of the metallic bar is magnified by the first lever in the proportion of the distances of the point of pressure from its plane, and from its other extremity ; and this magnified effect is again magnified by the other lever, so that an expansion of the 400th part of an inch corresponds to a whole inch on the scale. This pyrometer is liable to the objection that the distance of the points of pressure from the fulcrum and extremity of each lever is variable during the experiment. (See *Ferguson's Lect.*)

Mr Daniell has availed himself of the same property of expansion, in constructing a pyrometer, fig. 32, for measuring high degrees of heat. A bar of platinum is enclosed in a case (*a, b, c,*) made of the same ware as black lead crucibles, and is fixed to it at one end, while the other is left free to move an index *b* by which means degrees of heat above ignition admit of being accurately measured.

Pl. II.

The extremity *a*, is closed, the extremity, *c*, open ; *d*, is a ferule of brass into which the end of the black lead tube is accurately fitted, and to which the scale *e, f, g, h*, is attached. The bar of platinum (within the tube *a, b, c*, and extending to *b*,) is 10,2 inches long and 0,14 of an inch in diameter. It is immovably fixed at *a*, by a nut and screw of the same metal on the outside, and a pin or shoulder on the inside. It is likewise confined to its place at *b*, by a small perforated plate of platinum through which it passes. From its end *b* proceeds a fine platinum wire of about $\frac{1}{100}$ of an inch diameter, and coming out of the tube at *d* passes two or three times round the axis of the wheel *i*, fixed on the back of the scale *e, f, g, h*. It is then bent back and attached to the extremity of a slight spring *m, n*, which is stretched on the outside of the brass ferule, and fixed by a pin at *n* ; the wire is thus kept extended by the action of the spring. The axis of the wheel *i* is 0,062 of an inch in diameter, and the wheel itself is toothed, and plays into the teeth of another smaller wheel *k*. This smaller wheel is half the diameter of the larger, and carries on its circumference one third the number of teeth. To its axis, which passes through the centre of the scale, is attached the index *l*. The motion is multiplied three times by the wheel *k*. The scale is divided into 360°. It has been found preferable in practice to attach a short silken thread to the extremity of the platinum wire, and pass that round the axis of the wheel and fix it to the spring. See *Quarterly Journal*, xi. 309.

when heated from the freezing to the boiling point of water, suffer an increase in bulk=37,5 parts at mean pressure.

All bodies, after being heated, return again on cooling, precisely to their former dimensions.

The experiments of Gay Lussac have proved that steam and all vapours are subject to laws of expansion similar to those of air,—hence the table showing the changes of bulk suffered by 100000 parts of air at all temperatures between 32° and 212° will equally apply to all gases and vapours. *See Tables.*

Fluids with the highest boiling point expand most equally,

99. The expansion of liquids is not equable for equal additions of heat at different temperatures. Thus the addition of 5° of heat to alcohol at 40° , will produce a less relative increase of bulk than the same addition of heat to alcohol of 150° ; and in general, the nearer a liquid approaches its boiling point, the greater is its expansibility. Those liquids therefore appear most equably expansible which have the highest boiling points, and hence one of the great advantages of mercury, as will presently be seen, in constructing thermometers.

Specific gravity altered by a change of temperature.

100. As heat increases the bulk of all bodies, it is obvious that change of temperature is constantly producing changes in their density or specific gravity, as may be easily demonstrated in fluids where there is freedom of motion among the particles. If we apply heat to the bottom of a vessel of water, that portion of the fluid which is nearest to the source of heat, is expanded, and becoming specifically lighter, ascends, and is replaced by a colder portion from above. This, in its turn, becomes heated and dilated, and gives way to a second colder portion; and thus the process goes on, as long as the fluid is capable of imbibing heat. In air, similar currents are continually produced, and the vibratory motion observed over chimney pots, and slated roofs which have been heated by the sun, depends upon this circumstance: the warm air rises, and its refracting power being less than that of the circumambient colder air, the currents are rendered visible by the distortion of objects viewed through them.

Ventilation.

101. The ventilation of rooms and buildings, can only be perfectly effected by suffering the heated and foul air to pass off through apertures in the ceiling, while fresh air, of any desired temperature, is admitted from below. Various contrivances have been resorted to, to prevent the passage of cold air from above downwards through the ventilator, which can only be completely effected by keeping the ventilating tubes at a higher temperature than the surrounding air; heating them, for instance, by steam; passing them through a fire; or placing a lamp beneath them, of sufficient dimensions to cause a strong current upwards.

Exceptions to the law of expansion by caloric.

102. To the general law of the expansion of bodies by heat and their contraction by cold, there are, however, several exceptions. Water has attained its maximum of density at 40° , and if it be cooled below 40° it expands as the temperature

diminishes, as it does when heated above 40° ; and the rate of this expansion is equal for any number of degrees above or below its maximum of density, so that the bulk of water at 32° and at 48° will be the same. Accordingly, if two thermometer tubes, one containing spirit of wine, and the other water, be immersed into melting snow, the former will sink till it indicates 32° ; but the latter when it has attained 40° begins to expand, and continues to do so till it freezes. Or,

Fill a flask, capable of holding three or four ounces, with water at the temperature of 60° F. and adapt a cork to it, through which passes a glass tube open at both ends, about the eighth of an inch wide, and ten inches long. After having filled the flask, insert the cork and tube, and pour a little water into the latter till the liquid rises to the middle of it. On immersing the flask in a mixture of pounded ice and salt, the water will fall in the tube, marking contraction ; but in a short time an opposite movement will be perceived, indicating that expansion is taking place, while the water within the flask, is at the same time yielding caloric to the freezing mixture on the outside of it. Exp.

This anomaly in respect to water is productive of very important consequences, in preserving the depths of rivers and lakes of a temperature congenial to their inhabitants. An apparent object in this anomaly.

103. There are many liquids which suffer considerable expansion in passing into the solid state. This is the case with the greater number of saline solutions, and remarkably with water ; it seems connected with the phenomena of crystallization, and is referable to a new arrangement of particles. That the force with which water expands in the act of freezing is very considerable, is shown by the rupture of leaden and iron pipes in which it is suffered to freeze. Dr Thomson has shown that water in freezing suffers a much greater expansion than when heated from the freezing to the boiling point ; for the specific gravity of water at 60° being = 1, that of ice at 32° is only 0.92. Of the metals, Reaumur found that cast-iron, bismuth, and antimony, were expanded in becoming solid ; the rest contracted. Water expands more in freezing than it does when heated from the freezing to the boiling point.

104. The state of a body with respect to its power of producing the effects which arise from the operation of caloric, is termed its *temperature*. In every body the temperature depends on the quantity of caloric which it contains, and the temperature is said to be high or low as it respects another body, in proportion as it occasions an expansion or contraction of its parts. Temperature.

105. The temperature of bodies can be but imperfectly estimated by the sensation of heat or cold they produce, the sensation being modified by preceding impressions upon the sentient organ and other external circumstances. Hence the necessity of some common measure of temperature, as by means of the instrument called a *Thermometer*. imperfectly known from sensation.

106. The principle on which the thermometer indicates temperature, is, that caloric has a tendency always to preserve an equilibrium ; so that if two bodies at different temperatures, be brought into contact, it will pass from the one at the higher Principle on which the thermometer indicates temperature.

into that at the lower temperature, until the temperature of both is the same. Thus, if we mix equal quantities of the *same* fluid at different temperatures, the cold portion will expand as much as the hot portion contracts, and the resulting temperature is the mean; so that it appears, that as much heat as is lost by the one portion is gained by the other.

107. A common thermometer consists of a tube terminated at one end by a bulb, and closed at the other.* The bulb and part of the tube are filled with a proper liquid, generally mercury, and a scale is applied, graduated into equal parts. Whenever this instrument is applied to bodies of the same temperature, the mercury, being similarly expanded, indicates the same degree of heat. But when applied to bodies at different temperatures, the mercury will be most expanded by that which is at the highest temperature. We thus learn the difference in the temperature, but not the quantity of caloric the bodies contain. The difference is expressed numerically, namely, by the degrees of the thermometer.

Graduation
of thermom-
eters,

108. In dividing the scale of a thermometer, the two fixed points usually resorted to are the freezing and boiling of water, which always takes place at the same temperature, when under the same atmospheric pressure. The intermediate part of the scale is divided into any convenient number of degrees; and it is obvious, that all thermometers thus constructed will indicate the same degree of heat when exposed to the same temperature. In the centigrade thermometer, this space is divided into 100°; the freezing of water being marked 0°, the boiling point 100°. In this country we use Fahrenheit's scale, of which the 0° is placed at 32° below the freezing of water, which, therefore, is marked 32°, and the boiling point 212°, the intermediate space being divided into 180°. Another scale is Reaumur's; the freezing point is 0°, the boiling point 80°. These are the principal thermometers used in Europe and this country.

Rules for
comparing
the ordinary
thermome-
ters.

109. Each degree of Fahrenheit's scale is equal to $\frac{4}{9}$ ths of a degree on Reaumur's: if, therefore, the number of degrees on Fahrenheit's scale above or below the freezing of water be multiplied by 4 and divided by 9, the quotient will be the corresponding degree of Reaumur.

| Fahrenheit. | Reaumur. |
|---|--------------|
| $68^{\circ} - 32^{\circ} = 36 \times 4 = 144 \div 9 = 16^{\circ}$ | 16° |
| $212^{\circ} - 32^{\circ} = 180 \times 4 = 720 \div 9 = 80^{\circ}$ | 80° |

* The construction of a thermometer, though simple in theory, is difficult in practice, and it would be a vain attempt to make one from a written description. They are now constructed and circulated in such quantities as to be easily obtained. Those who prefer constructing their own, will find the process fully described in *Henry's Chemistry*, Vol. 1st, *Ure's Chemical Dictionary*, and in the *Journal of the Royal Institution*, Vol. 7th, p. 183.

Ordinary thermometers are frequently inaccurate, and many that are sufficiently correct for common purposes, are not so for delicate experiments. For the method of examining and correcting them, see *Faraday's Chemical Manipulation*, Section iv.

Directions for constructing thermometers of great sensibility, are given in the 7th vol. of the *Journal of Science*, p. 183.

To reduce the degrees of Reaumur to those of Fahrenheit, they are to be multiplied by 9, and divided by 4.

| | | |
|--|------------------|-------------|
| Reaumur. | | Fahrenheit. |
| $16^{\circ} \times 9 = 144 \div 4 = 36^{\circ}$ | $+ 32^{\circ} =$ | 68 |
| $30^{\circ} \times 9 = 720 \div 4 = 180^{\circ}$ | $+ 32^{\circ} =$ | 212 |

Every degree of Fahrenheit's is equal to $\frac{5}{9}$ ths of a degree on the centigrade scale; the reduction, therefore, is as follows:

| | | |
|--|--|-------------|
| Fahrenheit. | | Centigrade. |
| $212 - 32 = 180 \times 5 = 900 \div 9 = 100^{\circ}$ | | |
| Centigrade. | | Fahrenheit. |
| $100 \times 9 = 900 \div 5 = 180 + 32 = 212^{\circ}$ | | |

110. When a thermometer is intended to measure very low temperatures, spirit of wine is employed in its construction, as that fluid has never been frozen, whereas the low temperature at which it boils renders it unfit for measuring high temperatures. Quicksilver will indicate 500° , but freezes at -40° . Advantage of spirit of wine.

111. Air is sometimes resorted to as indicating very small changes of temperature. The instrument employed by Sanctorio, to whom the invention of the thermometer is generally ascribed, was of a very simple kind, and measured variations of temperature by the variable expansion of a confined portion of air. To prepare this instrument, a glass tube (fig. 12) is to be provided, eighteen inches long, open at one end, and blown into a ball at the other. On applying a warm hand to the ball, the included air expands, and a portion is expelled through the open end of the tube. In this state, the aperture is quickly immersed in a cup filled with any coloured liquid, which ascends into the tube, as the air in the ball contracts by cooling. The instrument is now prepared. An increase of temperature forces the liquor down the tube; and, on the contrary, the application of cold causes its ascent. These effects may be exhibited, by alternately applying the hand to the ball, and then blowing on it with a pair of bellows. By the application of a graduated scale, the amount of the expansion may be measured. Air thermometer of Sanctorio.

Pl. I.

The ball of this instrument, it must be obvious, cannot be conveniently applied to measure the temperature of liquids. For adapting it to this purpose, a slight variation may be made in its construction, as represented fig. 27. To prepare this instrument, a small spherical glass vessel is to be about one 6th or one 4th filled with any coloured liquid. The tube, open at both ends, is then to be cemented into the neck, with its lower aperture beneath the surface of the fluid. The expansion of the included air drives the liquid up the stem, to which we may affix a graduated scale, corresponding with that of a common mercurial thermometer. Other modifications have also been made by different philosophers. One of the most useful and simple forms is represented fig. 28. It consists merely of a tube of very small bore, from 9 to 12 inches long, at one end of which is blown a ball, from half an inch to an inch in diameter, which is afterwards blackened by paint, or by the smoke of a Air thermometer for liquids.

candle. A small column of coloured liquid, about an inch in length, is then introduced, by a manipulation similar to that already described. To fit the instrument for use, this column ought to be stationary, about the middle of the tube, at the common temperature of the atmosphere. The slightest variation of temperature occasions the movement of the coloured liquid; and a scale of equal parts measures the amount of the effect.

Objections to
their use,

An insuperable objection, however, to the air thermometer, *as thus constructed*, is, that it is affected, not only by changes of temperature, but by variations of atmospheric pressure. Its utility consists in the great amount of the expansion of air, which, by a given elevation of temperature, is increased in bulk above twenty times more than mercury. Hence it is adapted to detect minute changes of temperature, which the mercurial thermometer would scarcely discover, and its expansions being uniform for equal additions of heat, it is better adapted than any liquid for becoming, when properly applied, an accurate measure of temperature.

advantages.

Differential
thermometer

112. An important modification of the air thermometer was invented by Prof. Sturm^{ius}* and employed by Prof. Leslie, in his interesting researches respecting heat. To this instrument, he has given the name of the *Differential Thermometer*, fig. 13. It consists of two large glass bulbs containing air, united by a tube twice bent at right angles, containing coloured sulphuric acid. When a hot body approaches one of the bulbs, it drives the fluid towards the other. The great advantage of this instrument in delicate experiments is, that general changes of the atmosphere's temperature do not affect it, but it only indicates the *difference* of temperature between the two balls.

Howard's.

113. A differential thermometer has been contrived by Dr Howard resembling the above in its general form, fig. 16, but in which the degree of heat is measured by the expansive force of the vapour of ether or spirit of wine *in vacuo*. Directions for constructing it are given in the 8th vol. of the Quarterly Journal of Science, p. 219. It is intended to be applied to the same purposes as that of Prof. Sturm^{ius}, but is more sensible to changes of temperature, and the movement of the fluid (ether tinged by a drop of tincture of cochineal,) follows instantaneously the application of the heating cause, whereas in the air thermometer some time is required before the effect takes place. H. 1. 94.

Specific
caloric.

Capacity.

114. The relative quantities of heat which different bodies in the same state require to raise them to the same thermometric temperature, is called their *specific* heat, and those bodies which require most heat are said to have the greatest *capacity* for heat. That the quantity of heat in different bodies of the same temperature is different, was first shown by Dr Black, in his lectures at Glasgow in 1762.

* Brewster's Jour. 2. p. 145.

115. It has been stated (106) as a proof of the accuracy of the thermometer, that equal volumes of the same fluid, at different temperatures, give the arithmetical mean, on mixture. Thus, the temperature of a pint of hot and a pint of cold water is, after mixture, as near as possible half-way between the extremes. The cold water being of a temperature of 50° , and the hot of 100° , the mixture raises the thermometer to 75° . But if a pint of quicksilver at 100° be mixed with water at 50° , the resulting temperature is not 75° , but 70° ; so that the quicksilver has lost 30° , whereas the water has only gained 20° . Hence, it is said, that the *capacity* of mercury for heat is less than that of water; and if the weight of two bodies be compared, which are as 13,3 to 1, their capacities will be to each other as 19 to 1.*

116. It is important to know the specific caloric of bodies. The most convenient method of discovering it, is by mixing different substances together, and observing the relative quantities of caloric requisite for heating them by the same number of degrees. The caloric required to heat equal quantities of water, spermaceti oil, and mercury one degree, is in the ratio of 28,14 and 1, and therefore their capacities for caloric are expressed by those numbers. Water is commonly one of the materials employed in such experiments, as it is customary to compare the capacity of other bodies with that of water.†

Specific caloric how ascertained.

117. The capacities of bodies for heat have considerable influence upon the rate at which they are heated and cooled. Those bodies which are most slowly heated and cooled have generally the greatest capacity for heat. Thus, if equal quantities of water and quicksilver be placed at equal distances from the fire, the quicksilver will be more rapidly heated than the water, and the metal will cool most rapidly when carried to a cold place. Upon this principle, Professor Leslie ingeniously determined the specific heat of bodies, observing their relative times of cooling a certain number of degrees, comparatively with water, under similar circumstances.

Heating and cooling of bodies influenced by capacity.

Leslie's method.

M. M. Petit and Dulong have published some important researches on the subject of specific heat, which render it probable that the atoms of all simple substances have exactly the same capacities for heat.

All atoms seem to have the same capacity for caloric.

* The following is a general formula for determining the specific heat of bodies, from the temperature resulting from the mixture of two bodies at unequal temperatures, whatever be their respective quantities. Multiply the weight of the water by the difference between its original temperature and that of the mixture: also, multiply the weight of the other liquid by the difference between its temperature and that of the mixture: divide the first product by the second, and the quotient will express the specific heat of the other substance, that of water being = 1. Thus, 20 ounces of water at 105° , mixed with 12 ounces of spermaceti oil at 40° , produce a temperature of 90° . Therefore, multiply 20 by 15 (the difference between 105 and 90) = 300. And multiply 12 by 50 (the difference between 40 and 90) = 600. Then $300 \div 600 = \frac{1}{2}$, which is the specific heat of oil; that is, water being = 1, oil is = 0,5.

† This method was suggested by Dr Black, and afterwards practised to a great extent by Drs Crawford and Irvine. See Crawford on *Animal Heat*, and Irvine's *Essays*.

Lavoisier's
method.

118. Lavoisier and Laplace endeavoured to ascertain the specific heat of bodies by the relative quantities of ice which they were capable of thawing, during cooling: thus, if a pint of water in cooling from 212° to 32° melted a pound of ice, and a pint of oil in passing through the same range of temperature only gave out heat enough to thaw half a pound of ice, it was concluded that the specific heat of water being = 1, that of the oil was = 0,5. The instrument which they employed in these researches, and which is fully described in Lavoisier's *Elements of Chemistry*, is not however, susceptible of accuracy, for Mr Wedgwood has shown that it is scarcely possible to separate the water from the ice.—*Phil. Trans.* Vol. lxxiv.

Dilatation of
gases pro-
duces cold,
compression
heat.

119. The capacity of gases and vapours differs with the nature of the gas, and with its density. In gases, dilatation produces cold, and compression excites heat. A thermometer suspended in the receiver of the air-pump sinks during exhaustion, and sudden compression of air produces heat sufficient to inflame tinder. In liquids, too, condensation diminishes capacity for heat; hence the mixture of spirit and water, and of sulphuric acid and water evolves heat (53). The increased capacity which air acquires by rarefaction has its influence in modifying natural temperatures. The air, becoming rarer as it ascends, absorbs its own heat and hence becomes cold in proportion as it recedes from the earth's surface: thus moisture, rain, or snow are thrown down on the mountain-tops.

Radiant calo-
ric.

120. Caloric escapes from bodies in two different modes.—Part of it finds its way through space, independently of other matter, and with immeasurable velocity. In this state it has been called radiant heat, or radiant caloric.

Reflection
of caloric.

121. Radiant caloric exhibits several interesting properties. 1. Its reflection. Those surfaces, that reflect light most perfectly, are not equally adapted to the reflection of caloric. Thus, a glass mirror, which reflects light with great effect when held before a blazing fire, scarcely returns any heat, and the mirror itself becomes warm. On the contrary, a polished plate of tin, or a silver spoon, when similarly placed, reflects, to the hand, a very sensible degree of warmth; and the metal itself remains cool. Metals, therefore, are much better reflectors of caloric than glass; and they possess this property, exactly according to their degree of polish.

122. Caloric is reflected according to the same law that regulates the reflection of light. This is proved by an interesting experiment of M. Pictet; the means of repeating which may be attained at a moderate expense. Provide two reflectors of planished tin, (*a* and *b*, fig. 24,) which may be 12 inches diameter, and segments of a sphere nine inches radius. Parabolic mirrors are still better adapted to the purpose, but their construction is less easy. Each of these must be furnished, on its convex side, with the means of supporting it in a perpendicular position on a proper stand. Place the mirrors opposite

to each other on a table, at the distance of from six to twelve feet. Or they may be placed in a horizontal position, as represented in the fourth plate to Sir H. Davy's Chemical Philosophy, an arrangement in some respects more convenient. In the focus of one, let the ball of an air thermometer, or (which is still better) one of the balls of a differential thermometer, be situated; and in that of the other, suspend a ball of iron, about four ounces in weight, and heated below ignition, or a small matrass of hot water; having previously interposed a screen before the thermometer. Immediately on withdrawing the screen the depression of the column of liquid, in the air thermometer, evinces an increase of temperature in the instrument. In this experiment, the caloric flows first from the heated ball to the nearest reflector; from this it is transmitted, in parallel rays, to the surface of the second reflector, by which it is collected into a focus on the instrument. This is precisely the course that is followed by radiant light; for if the flame of a taper be substituted for the iron ball, the image of the candle will appear precisely on that spot, (a sheet of paper being presented for its reception,) where the rays of caloric were before concentrated. H. 1. 102.

123. If a plate of glass be interposed between the two mirrors, the rays of heat will be arrested, while those of light freely passing through the glass will be collected as usual in the opposite focus. This, therefore shows a difference between solar and terrestrial heat; the rays of the former pass through glass without heating it; the rays of the latter are stopped by glass, and it becomes hot when opposed to them.*

124. When a glass vessel, filled with ice or snow, is substituted for the heated ball, the course of the coloured liquid in the thermometer will be precisely in the opposite direction; for its ascent will show, that the air in the ball is cooled by this arrangement. This experiment, which appears, at first view, to indicate the reflection of cold, presents, in fact, only the reflection of heat in an opposite direction; the ball of the thermometer being, in this instance, the hotter body.

Apparent
radiation
of cold.

125. Radiation goes on in all elastic media, and in the Torricellian and air-pump vacuum, as may be shown by igniting charcoal by means of the Voltaic battery, placed in the focus of a small mirror confined in the exhausted receiver of the air-pump. Sir H. Davy found that the receiver being exhausted to $\frac{1}{120}$, the effect upon the thermometer in the opposite focus was nearly three times as great as when the air was in its natural state of condensation, fig. 19. *a* is the receiver, *bb* the insulated wires connected with the voltaic apparatus igniting the charcoal in the focus of the upper mirror *c*. In the focus of the lower mirror *d* is the thermometer *e*.

Radiation in
elastic media
and the Tor-
ricellian va-
cuum.

Pl. 1.

126. The facts that have been determined concerning the laws of radiant caloric have given rise to several modes of accounting for the tendency of bodies to acquire an equilibrium of tempera-

Theories.

* Schoele's Experiments on Air and Fire.

Pictet's.

ture. This takes place, according to M. Pictet, in consequence of the hot body giving calorific rays to the surrounding colder ones till an equilibrium is established, at which moment the radiation ceases. M. Prevost, on the contrary, contends that radiation goes on at all times, and from all bodies, whether their temperature is the same or different from those that surround them. According to this view, the temperature of a body falls whenever it radiates more caloric than it absorbs; its temperature is stationary when the quantities emitted, and received are equal; and it becomes warm when the absorption exceeds the radiation.

Leslie's.

127. Professor Leslie* accounts for radiation upon the idea of the heated body producing undulations in the air, somewhat analogous to the waves excited by sonorous bodies; others with Mr Brande regard matter in motion as the cause of the effect, and conceive that the phenomena both of solar and terrestrial radiation are most satisfactorily explained upon such an hypothesis.

128. The nature of the *surface* of bodies has an important influence over their power of *radiating* caloric.

Heating effect of solar rays with regard to superficial colours.

129 It has long been known, in regard to solar rays, that their heating effect depends much upon the colour of the surfaces upon which they impinge, and that black and dark bodies are more heated than those which are white or of light tints, circumstances dependent upon absorption and reflection.

Exp.

To exhibit this influence experimentally, let a canister of planished block tin, forming a cube of six or eight inches, be provided, having an orifice at the middle of its upper side, from half an inch to an inch diameter, and the same in height. This orifice is intended to receive a cap having a small hole, through which a thermometer is inserted, so that its bulb may reach the centre of the canister. Let one side of the canister be covered with black paint; destroy the polish of another side, by scratching it with sand-paper; tarnish a third with quicksilver; and leave the fourth bright. Then fill the vessel with boiling water. The radiation of caloric from the blackened side is so much more abundant than from the others, as to be even sensible to the hand. Place it before a reflector (fig. 24) in lieu of the heated iron ball already described. The thermometer, in the focus of the second reflector, will indicate the highest temperature, or most copious radiation of caloric, when the blackened side is presented to the reflector; less, when the tarnished or scratched side is turned towards it; and least of all from the polished side. H.

Pl. I.

Radiation of caloric in direct proportion to its degree of absorption.

130. In these experiments nearly the whole of the heat is reflected, and the mirror itself does not become warm: but if it be coated with any unpolished, and especially unmetallic coating, as with paper, or paint, the reflection is then scarcely perceptible, and the mirror becomes hot from the absorption of the radiant caloric.

* See Leslie; *Experimental Inquiry into the nature and propagation of heat.*

In Professor Leslie's experiments it was found, that a clean metallic surface produced an effect = 12 upon the thermometer. When covered with a thin coat of glue, its radiating power was so far increased as to produce an effect = 80 ; and on covering it with lamp-black, it became = 100.

In these cases of radiation, the *colour* of the surface does not interfere, and the different effects must be referred to the mechanical structure of the radiating surface. White paper and lamp-black produce nearly the same effects ; and paper, coloured blue, red, yellow, and green, does not differ in radiating power from that which is white, provided the colour produces no change of texture in the paper.

Radiation independent of superficial colour.

131. The connexion of the receptive with the radiating power is made obvious by coating the bulbs of thermometers with different substances. Thus the effect of radiant heat upon a thermometer bulb covered with a thin coating of lamp-black being = 100 ; when the bulb is covered with silver-leaf the effect is only = 12.*

132. The varieties in the radiating power of different surfaces, are attended, as might be expected, with corresponding variations in the *rate of cooling*. If water in a tin vessel, all of whose sides are polished, cools through a given number of degrees in eighty-one minutes, it will descend through the same number in seventy-two minutes, if the surface be tarnished with quicksilver. Water, also, enclosed in a clean and polished tin ball, cools about twice more slowly than water in the same ball covered with oiled paper. Blackening the surface with paint, or even a thin coat of varnish, on the same principle, (128) accelerates greatly the rate of cooling. H. 1. 104.

Rate of cooling influenced by difference of surface.

It is obvious, from these facts, that all vessels intended to retain heat, should be clean, and metallic, for polished metallic surfaces have very low radiating powers ; whereas those vessels which are either to receive, or to radiate, should be blackened upon their surfaces. The knowledge of these properties is economically applicable in a variety of cases.

Vessels intended to retain caloric should be clean and metallic.

133. Radiant caloric is *absorbed* with different facility by different surfaces. This is only stating, in other terms, that surfaces are endowed with various powers of reflecting caloric, since the power of absorbing caloric is precisely opposite to that of reflecting it. Hence the best reflectors of heat will absorb the least. It may be proper, however, to offer some illustrations of the principle under this form.

Absorption of caloric influenced by surface.

Expose the bulb of a sensible thermometer to the direct rays of the sun. On a hot summer's day it will probably rise, in this climate, (Eng.) to 108° .† Cover it with India ink, and again expose it in a similar manner. During the evaporation of the moisture, it will fall ; but as soon as the coating becomes dry, it will ascend to 118° , or upwards, of Fahrenheit, or 10°

Exp.

* M. M. Dulong and Petit, in their valuable *Memoir on Heat*, which gained the prize-medal of the Academy of Sciences for 1818, have detailed a variety of important facts upon the subject of the radiation of surfaces.

† Watson's *Essays*, v. 152.

higher than when uncovered with the pigment. This cannot be explained by supposing that the black coating is gifted with the power of retaining caloric, and preventing its escape ; because, from experiments already related, it appears, that a similar coating accelerates the cooling of a body to which it is applied.

134. Colour has considerable influence over the absorption of caloric. This is shown by the following very simple experiment of Dr Franklin.

Absorption
of caloric in-
fluenced by
colour.

Exp.

On a winter's day, when the ground is covered with snow, take four pieces of woollen cloth, of equal dimensions, but of different colours, viz. black, blue, brown, and white, and lay them on the surface of the snow, in the immediate neighbourhood of each other. In a few hours, the black cloth will have sunk considerably below the surface ; the blue almost as much ; the brown evidently less ; and the white will remain precisely in its former situation.

Thus it appears that the sun's rays are absorbed by the dark coloured cloth, and excite such a durable heat, as to melt the snow underneath ; but they have not the power of penetrating the white. Hence the preference, generally given to dark coloured clothes during the winter season, and to light coloured ones in summer, appears to be founded on reason. H. 105.

Conducting
power of bo-
dies for calo-
ric.

135. When different bodies are exposed to the same source of heat, they suffer it to pass through them with very different degrees of velocity or they have various *conducting powers* in regard to heat. Among solid bodies, metals are the best conductors ; and silver, gold, tin and copper, are better conductors than platinum, iron, and lead. Next to the metals, we may, perhaps, place the diamond, and topaz ; then glass ; then siliceous and hard stony bodies in general ; then soft and porous earthy bodies, and wood ; and lastly, down, feathers, wool, and other porous articles of clothing.

Method of de-
termining this
power.

Exp.

136. To compare the relative conducting powers of metals, and some other solids, small cones of the different substances may be used about three inches high, and half an inch in diameter at their bases : these may be tipped at the apex with a small piece of wax, and being placed on a heated metallic plate, will indicate the conducting powers by the relative times required to fuse the wax, which will be inversely, as the power of conducting heat.*

The difference between the conducting power of the diamond and rock crystal or glass, is shown by applying the tongue to those substances, when the former feels colder than the latter.†

* This experiment may be varied by attaching small pieces of phosphorus to the cones.

† From the experiments of Professor Mayer, of Erlangen, (*Annales de Chimie*, tom. xxx) it would appear that the conducting powers of different woods are in some measure inversely as their specific gravities, as shown by the following table, water being assumed as = 1.

Table of con-
ducting pow-
ers of woods.

| | Conducting Power. | Specific Gravity. | | Conducting Power. | Specific Gravity. |
|------------|----------------------|----------------------|---------------|----------------------|----------------------|
| Water | 10 | 1,000 | Oak | 32,6 | 0,668 |
| Ebony Wood | 21,7 | 1,054 | Pear tree | 33,2 | 0,603 |
| Apple tree | 27,4 | 0,639 | Birch | 34,1 | 0,608 |
| Ash | 30,8 | 0,631 | Silver fir | 37,5 | 0,495 |
| Beech | 32,1 | 0,692 | Alder | 38,4 | 0,484 |
| Hornbeam | 33,3 | 0,690 | Scotch fir | 38,6 | 0,403 |
| Plum tree | 33,5 | 0,687 | Norway Spruce | 38,9 | 0,447 |
| Elm | 32,5 | 0,646 | Lime | 39,0 | 0,403 |

Count Rumford's experiments on the conducting power of several substances used as clothing, offer some interesting results.* Conducting power of clothing substances. He found that a thermometer enclosed in a tube and bulb of the same shape, but large enough to allow of an inch vacant space between the two, being previously heated, required 576 seconds to cool 135° . When 16 grains of lint were diffused through the confined air, it took 1032 seconds to undergo the same change of temperature; and 1305 seconds, with the same weight of Eider-down. The compression of flocculent substances to a certain extent, renders them still inferior conductors: thus, when the space which in the above experiments contained 16 grains of Eider-down was filled with 32, and then with 64 grains, the times required for the escape of 60 degrees of heat were successively increased from 1305'' to 1472'' and 1615''.

On the other hand to show the effect of mere *texture*, similar comparative trials were made of the conducting powers of equal weights of raw silk, of ravellings of white taffeta, and of common sewing silk, of which the first has the finest fibre, the second less fine, and the third from being twisted and harder is much coarser. The difference between these three modifications of the same substance is very striking, the raw silk detaining the heat for 1824'', the taffeta ravellings 1469'', and the silk thread only 947''.† Effect of texture.

137. The different conducting powers of bodies in respect to heat, are shown in the application of wooden handles to metallic vessels; or a stratum of ivory or wood is interposed between the hot vessel and the metal handle. The transfer of heat is thus prevented. Heat is confined by bad conductors; hence clothing for cold climates consists of woollen materials; hence, too, the walls of furnaces are composed of clay and sand.—Confined air is a very bad conductor of heat; hence the advantage of double doors to furnaces, to prevent the escape of heat; and of a double wall, with an interposed stratum of air, to an icehouse, which prevents the influx of heat from without. Practical application.

138. From the different conducting powers of bodies in respect to heat, arise the sensations of heat and cold experienced upon their application to our organs, though their thermometric temperature is similar. Good conductors occasion, when touched, a greater sensation of heat and cold than bad ones. Metal feels cold because it readily carries off the heat of the body; and we cannot touch a piece of metal immersed in air of a temperature moderate to our sense. Sensations of heat and cold.

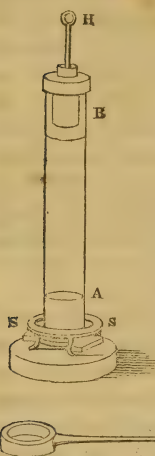
139. Liquids and gases are very imperfect conductors of heat, and heat is generally distributed through them by a change of specific gravity; by an actual change in the situation of their particles. (100.) Liquids and gases imperfect conductors.

Take a glass tube, ten or twenty inches long, and four or six in diameter. Exp. Pour into the bottom part, for about the depth of five inches, water tinged

* Phil. Trans. 1792.

* Aikin's Diet. Art. Caloric.

with litmus, or cabbage, and fill up the tube with common water, pouring on the latter extremely gently, so as to keep the two strata quite distinct. If the upper part of the tube be first heated, the coloured liquor will remain at bottom; but if the tube be afterwards heated at bottom, the infusion will ascend, and will tinge the whole mass of fluid.



Exp.

A convenient method of exhibiting this has been contrived by Dr Hare. A glass jar, about 30 inches in height, is supplied with as much colourless water as will rise in it within a few inches of the brim. By means of a tube descending to the bottom, a small quantity of blue colouring matter is introduced *below* the colourless water, so as to form a stratum, as represented at A in the annexed cut. A stratum differently coloured, is formed in the upper part of the vessel, as at B. A tin cap, supporting a hollow tin cylinder, closed at bottom, and about an inch less in diameter than the jar, is next placed as it is seen in the figure, so that the cylinder may be concentric with the jar, and descend about 3 or 4 inches into the water. If an iron heater H while red hot, be placed within the tin cylinder, the coloured water about it will soon boil; but the heat penetrates only a very small distance below the tin cylinder, so that the colourless water, and the coloured stratum, at the bottom of the vessel, remain undisturbed, and do not mingle. But if an iron ring be placed while red hot, upon the iron stand which surrounds the jar at S, S, the liquid soon rises, in beautiful clouds, until it encounters the warmer and lighter particles which had been in contact

with the tin cylinder.*

Exp.

Fill a jar with hot water; and place a cake of ice on the surface of the water. The ice will soon be melted. This experiment is the more striking, if the water, used for forming the cake of ice, be previously coloured with litmus; for, the descending currents of cold water are thus made apparent.

Substituting water of the temperature of 11° for the boiling water used in this experiment, Count Rumford found, that, in a given time, a much greater quantity of ice was melted by the cooler water. This appears, on first view, rather paradoxical. The fact, however, is explained by the remarkable property of water, *viz.* that, when cooled below 40° , it ceases to contract, and experiences on the contrary, an enlargement of bulk. Water, therefore, at 40° , (at the bottom of which is a mass of ice at 32° .) is cooled by contact with the ice, and is expanded at the same moment. It therefore ascends, and is replaced by a heavier and warmer portion from above.

140. It is a consequence of the same property, that the surface of a deep lake is sometimes covered with ice, even when the water below is only cooled to 40° ; for the superficial water is specifically lighter than the warmer water beneath it, and retains its place, till it is changed into ice. This property of water is one of the most remarkable exceptions to the law of expansion. (103.)

Rumford's
experiments.

141. From the fact that heat applied to the upper surface of water, will with difficulty make its way downwards, (139), Count Rumford was induced to deny that water could conduct at all.

Exp.
Pl. 1.

Let an air thermometer be cemented into a glass funnel supported as represented in fig. 14; cover the bulb of the instrument with water, and upon the surface of the water pour a small quantity of ether. The ether may be inflamed and the air thermometer will not be sensibly affected.

* From Dr. Hare's *Engravings and description of Chemical Apparatus*, &c. Part 1st, page 41.

Count Rumford inferred that fluids propagate caloric only in one direction, viz. upwards in consequence of the motions which it occasions among the particles of fluid, and that if these motions could be suspended, caloric would cease to pass through water. With the view of deciding this question, he made the following experiments.

Provide a cylindrical tin vessel, two inches in diameter, and $2\frac{1}{2}$ inches deep, Exp. having a moveable cover, perforated with a small aperture, for transmitting the stem of a thermometer, which is to be inserted, so that its bulb may occupy the centre of the vessel.

Fill this vessel with water of the temperature of the atmosphere; let the cover be put in its place; and let the whole apparatus, except the scale of the thermometer, be immersed in water, which is to be kept boiling over a lamp. Observe how long a time is required to raise the water from its temperature at the outset to 180° , and remove it from its situation. Note, also, how long it takes to return to its former temperature.

Repeat the experiment, having previously dissolved in the water 200 grains Exp. of common starch. The thermometer will now require about half as long again to arrive at the same temperature. A similar retardation, and to a greater amount, is produced by the mixture of eider-down, cotton-wool, and various other substances, which are not chemically soluble in water, and which can diminish its conducting power in no other way than by obstructing the motion of its particles.*

142. The inference that water is a complete non-conductor of caloric has been contradicted by the subsequent inquiries of Dr Hope, Dr Thompson, and the late Dr Murray. Though they all admit that water and liquids in general, mercury excepted, possess the power of conducting caloric in a very slight degree. The following experiment made by Dr Murray has been deemed conclusive.† Fluids imperfect conductors.

If we carefully pour hot oil upon water in a tall glass jar, with delicate thermometers placed at different distances under the surface, it will be found that those near the heated surface indicate increase of temperature. Exp.

It might here be said that the heat was conducted by the sides of the jar, and so communicated to the water; to obviate such objection Dr Murray made the experiment in a vessel of ice, which being converted into water at 32° , cannot convey any degree of heat above 32° downwards; yet the thermometers were affected, as in the former trial.‡

143. Experiments on the conducting power of air are complex and difficult, and the results hitherto obtained are unsatisfactory. Air.

144. Heat has great influence on the *forms* or *states* of bodies. When we heat a solid it becomes fluid or gaseous, and liquids are converted into æriform bodies or vapours. Dr Black investigated this effect of heat with singular felicity, and his researches rank among the most admirable efforts of experimental philosophy.§ During the liquefaction of bodies, a quantity of heat is absorbed, which is essential to the state of fluidity, Forms and states of bodies influenced by caloric.

Liquefaction.

* Rumford's *Essays*.

† *System of Chemistry*, vol. i. p. 319.

‡ Several ingenious experiments have been lately made by Mr Mather, (*Amer. Jour.* vol. xiii. p. 308,) which render it probable that this effect may be partly owing to *radiation*.

§ *Black's Lectures*, edited by John Robison, LL. D.

and which does not increase the sensible or thermometric temperature. Consequently, if a cold solid body, and the same body hot and in a liquid state, be mixed in known proportions, the temperature after mixture will not be the proportional mean, as would be the case if both were liquid, but will fall short of it; much of the heat of the hotter body being consumed in rendering the colder solid, *liquid*, before it produces any effect upon its *sensible temperature*.

Latent caloric.

145. Equal parts of *water* at 32° , and *water* at 212° will produce on mixture a mean temperature of 122° . But equal parts of *ice* at 32° , and *water* at 212° , will only produce (after the liquefaction of the ice) a temperature of 52° , the greater portion of the heat of the water being employed in thawing the ice, before it can produce any rise of temperature in the mixture. To heat thus *insensible* or *combined*, Dr Black applied the term *latent heat*. The actual loss of the thermometric heat in these cases was thus estimated; a pound of ice at 32° was put into a pound of water at 172° ; the ice melted, and the temperature of the mixture was 32° . Here the water was cooled 140° , while the *temperature* of the ice was unaltered; that is, 140° of heat disappeared, their effect being not to increase temperature, but to produce fluidity.

Cold produced by rapid solution.

146. In all cases of liquefaction caloric is absorbed, and we produce artificial cold, often of great intensity, by the rapid solution of certain saline bodies in water. Upon this principle the action of freezing mixtures depends, some of which may frequently be conveniently and economically applied to the purpose of cooling wine or water in hot climates, or where ice cannot be procured.

Exp.

Dilute a portion of nitric acid with an equal weight of water; and, when the mixture has cooled, add to it a quantity of light fresh-fallen snow. On immersing the thermometer in the mixture, a very considerable reduction of temperature will be observed. This is owing to the absorption, and intimate fixation of the free caloric of the mixture by the liquefying snow.

Exp.

Mix quickly together equal weights of fresh-fallen snow at 32° , and of common salt, cooled, by exposure to a freezing atmosphere, down to 32° . The two solid bodies, on admixture, will rapidly liquefy; and the thermometer will sink 32° , or 0; or, according to Sir C. Blagden, to 4° lower.*

To understand this experiment, it must be recollected, that the snow and salt, though at the freezing temperature of water, have each a considerable portion of uncombined caloric. Now salt has a strong affinity for water; but the union cannot take place while the water continues solid. In order, therefore, to act on the salt, the snow absorbs all the free caloric required for its liquefaction; and during this change, the free caloric, both of the snow and the salt, amounting to 32° , becomes latent, and is concealed in the solution. This solution remains in a liquid state at 0, or 4° below 0 of Fahrenheit; but if a greater degree of cold be applied to it, the salt separates in a concrete form.

* *Philosophical Transactions*, lxxviii. 281.

Most neutral salts, also, during solution in water, absorb much caloric ; and the cold, thus generated, is so intense as to freeze water, and even to congeal mercury. The former experiment, however, (viz. the congelation of water,) may easily be repeated on a summer's day.

Add to 32 drachms of water, 11 drachms of muriate of ammonia, 10 of nitrate of potash, and 16 of sulphate of soda, all finely powdered. The salts may be dissolved separately, in the order set down. A thermometer, put into the solution, will show, that the cold produced is at, or below, freezing ; and a little water, in a thin glass tube, being immersed in the solution, will be frozen in a few minutes. H. 1. 113.*

Exp.

147. Crystallized muriate of lime, when mixed with snow, produces a most intense degree of cold. This property was discovered some years ago by M. Lovitz, of St. Petersburg, and has been since applied to the congelation of mercury on a very extensive scale. The proportions, which answer best, are about equal weights of the salt finely powdered, and of fresh-fallen and light snow. On mixing these together, and immersing a thermometer in the mixture, the mercury sinks with great rapidity. For measuring exactly the cold produced, a spirit thermometer, graduated to 50° below 0 of Fahrenheit, or still lower should be employed. A few pounds of the salt are sufficient to congeal a large mass of mercury. By means of 13 pounds of the muriate, and an equal weight of snow, Messrs Pepys and Allen froze 56 pounds of quicksilver into a solid mass. The mixture of the whole quantity of salt and snow, however, was not made at once, but part was expended in cooling the materials themselves.

Method of freezing mercury.

On a small scale, it may be sufficient to employ two or three pounds of the salt. Let a few ounces of mercury, in a very thin glass retort, be immersed, first in a mixture of one pound of each ; and, when this has ceased to act, let another similar mixture be prepared. The second will never fail to congeal the quicksilver.†

148. When fluids are converted into solids, their *latent* heat becomes *sensible*. Water if kept perfectly free from agitation may be cooled down several degrees below 32° ; but, on shak-

Latent caloric made sensible.

* The results of some of Mr Walker's experiments on this subject, are given in the table of freezing mixtures in the Appendix.

† In fig. 33, a very simple and cheap apparatus is represented, which may be employed to freeze mercury. The outer vessel of wood may be twelve and a half inches square, and seven inches deep. It should have a wooden cover, rabbeted in, and furnished with a handle. Within this is placed a tin vessel *b b*, standing on feet which are one and a half inches high, and having a projection at the top, half an inch broad and an inch deep, on which rests a shallow tin pan *c c*. Within the second vessel is a third *d*, made of untinned iron, and supported by feet two inches high. This vessel is four inches square, and is intended to contain the mercury. When the apparatus is used, a mixture of muriate of lime and snow is put into the outer vessel *a a*, so as completely to surround the middle vessel *b b*. Into the latter, the vessel *d*, containing the quicksilver to be frozen, previously cooled down by a freezing mixture, is put ; and this is immediately surrounded by a mixture of snow and muriate of lime, previously cooled to 0° Fahrenheit, by an artificial mixture of snow and common salt. The pan *c c* is also filled with these materials, and the wooden cover is then put into its place. The vessels are now left till the quicksilver is frozen. A more elegant, but more expensive, apparatus, by Mr Pepys, intended for the same purpose, is figured in an early volume of the Philosophical Magazine. H. 1. 114. Pl. 2.

ing it, it immediately congeals, and the temperature rises to 32° .

149. The evolution of caloric, during the congelation of water is well illustrated by the following experiment of Dr Crawford.

Exp. Into a round tin vessel put a pound of powdered ice ; surround this by a mixture of snow and salt in a larger vessel ; and stir the ice in the inner one, till its temperature is reduced to $+ 4^{\circ}$ Fahrenheit. To the ice thus cooled add a pound of water at 32° . One-fifth of this will be frozen ; and the temperature of the ice will rise from 4° to 32° . In this instance, the caloric evolved, by the congelation of one fifth of a pound of water, raises the temperature of a pound of ice 28° . H. 1. 115.

Exp. Dissolve sulphate of soda in water, in the proportion of one part to five, and surround the solution by a freezing mixture, it will cool gradually down to 31° . The salt, at this point, begins to be deposited, and stops the cooling entirely.

This evolution of caloric during the separation of a salt, is exactly the reverse of what happens during its solution.*

When a solution of Glauber's salt is made suddenly to crystallize, its temperature is considerably augmented ; (34) and when water is poured upon quicklime, a great degree of heat is produced by the solidification which it suffers in consequence of chemical combination ; congelation, therefore, is to surrounding bodies a heating process, and liquefaction a cooling process.

Conversion
of liquids into
the aëriform
state.

150. When liquids are heated they acquire the gaseous form, and become invisible elastic fluids, possessed of the mechanical properties of common air. This effect of caloric is termed *Vaporization*. They retain this form or state as long as their temperature remains sufficiently high, but re-assume the liquid form when cooled again.

Exp. Fill a jar with water heated to 104° and invert it in a vessel of the same. Then introduce a little ether by means of a glass tube closed at one end. The ether will rise to the top of the jar, and, in its ascent will be changed into gas, filling the whole jar with a transparent, invisible, elastic fluid. On permitting the water to cool, the ethereal gas is condensed, and the inverted jar again becomes filled with water.

Boiling point
of liquids dif-
ferent.

X 151. The temperature at which vapour rises with sufficient freedom for causing the phenomena of ebullition, is called the boiling point. The heat requisite for this effect varies with the nature of the fluid. Thus sulphuric ether boils at 96° F. alcohol at 173° and pure water at 212° ; while oil of turpentine must be raised to 316° , and mercury to 660° before either exhibits marks of ebullition. The appearance of boiling is owing to the formation of vapour at the bottom of the vessel, and its escape through the heated fluid above it.

Boiling point
constant un-
der some cir-
cumstances.

152. The boiling point of the same liquid is constant, so long as the necessary conditions are preserved ; but it is liable to be affected by several circumstances. The nature of the vessel has some influence upon it. Thus Gay Lussac observed that pure water boils precisely at 212° in a metallic vessel and at 214° in one of glass. It is likewise affected by the presence of foreign substances. Dr Bostock found that ether, heated in a glass

* Blagden, *Philos. Trans.* lxxviii. 290.

vessel, had its boiling point lowered nearly 50° by introducing a few chips from a cedar pencil, and alcohol of s. g., 849 had its boiling point reduced by a similar cause between 30° and 40° . The boiling point of water, heated in a glass vessel, was brought down 4° or 5° by the same means.* By putting coils of wire into liquids, heated in glass vessels with a view to distillation, they are made to boil readily, quietly and some degrees lower than they would otherwise do. It is of course necessary to use a metal which will not be acted upon by the liquid.

Influenced by circumstances.

153. A circumstance which has great influence over the boiling point and vaporization of fluids is variation of pressure. By the mere removal of atmospheric pressure ether will be converted into vapour at the common temperature of the atmosphere.

Effect of pressure

Into a glass tube, fig. 10, about six inches long, and half an inch in diameter, put a teaspoonful of ether, and fill up the tube with water; then, pressing the thumb on the open end of the tube, place it, inverted, in a jar of water. Let the whole be set under the receiver of an air-pump, and exhaust the air. The ether will be changed into gas, which will expel the water entirely from the tube. On re-admitting the air into the receiver, the gas is again condensed into a liquid form.

Exp.

154. From the experiments of the late Prof. Robison it appears that liquids boil in a vacuum at a temperature 140° lower than in the open air.† Thus water boils at 72° F., alcohol at 33° and ether at -44° . This proves that a liquid is not necessarily hot because it boils. The heat of the hand is sufficient to make ether boil in a vacuum, as is exemplified by the *Pulse glass*.

Boiling point in vacuo.

155. Even the ordinary variations in the weight of the air, as measured by the barometer, are sufficient to make a difference in the boiling point of water of several degrees. When the barometer is at 28 inches, water will boil at the temperature of $208,43^{\circ}$, when at 30 inches at 212 , and when at 31 at $213,76^{\circ}$. At the top of Mount Blanc, Saussure found that it boiled at 187° , so that the heights of mountains, and even of buildings, may be calculated by reference to the temperature at which water boils upon their summits. The Reverend Mr Wollaston has described to the Royal Society the method of constructing a thermometer of extreme delicacy, applicable to these purposes.‡

Effect of changes of density of the air.

Altitudes determined by the changes in the boiling points of water.

156. The following apparently paradoxical experiment also illustrates the influence of diminished pressure in facilitating ebullition.

Example of diminished pressure facilitating ebullition.

Insert a stopcock securely into the neck of a Florence flask, fig. 18, containing a little water, and heat it over a lamp till the water boils, and the steam freely escapes by the open stopcock; then suddenly remove the lamp and close the cock. The water will soon cease to boil; but if plunged into a vessel of cold water ebullition instantly recommences, but ceases if the flask be held near the fire: the vacuum in this case being produced by the condensation of the steam.

Exp.

157. Water cannot be heated under common circumstances beyond 212° F. because it then acquires such an expansive

Example of the contrary effect of pressure.

* Ann. of Philos. N. S. ix. 196.

† Black's Lectures, Vol. 1, p. 151.

‡ Phil. Trans. 1817.

1. 2.

force as enables it to overcome the atmospheric pressure, and to fly off in the form of vapour. But if subjected to sufficient pressure, it may be heated to any extent without boiling. For making experiments on this subject the apparatus, represented plate 2. fig. 39, contrived by Dr Marcet, will be found extremely useful. *a* is a strong brass globe, composed of two hemispheres screwed together with flanches; a portion of quicksilver is introduced into it, and it is then about half filled with water. *b* is a barometer-tube passing through a steam-tight collar, and dipping into the quicksilver at the bottom of the globe. *c* is a thermometer graduated to about 400° , and also passing through an air-tight collar. *d* is a stopcock, and *e* a large spirit lamp. The whole is supported upon the brass frame and stand *f*. Upon applying heat to this vessel, the stopcock being closed as soon as the water boils, it will be found that the temperature of the water and its vapour increases with the pressure, which is measured by the ascent of the mercury in the barometer-tube. The thermometer under atmospheric pressure being at 212° , will be elevated to 217° under a pressure of five inches of mercury, and to 242° under a pressure of 30 inches, or thereabouts; each inch of mercury producing by its pressure, a rise of about 1° in the thermometer. The barometer-tube also serves the purpose of a safety-valve, the strength of the brass globe being such as to resist a greater pressure than that of one atmosphere.

Sensible or
free caloric
made latent.

158. The conversion of a liquid into vapour is always attended with great loss of thermometric heat; and as liquids may be regarded as compounds of solids and heat, so vapours may be considered as consisting of a similar combination of heat with liquids; in other words, a great quantity of heat becomes latent during the formation of vapour.

Exp.

Moisten a thermometer with alcohol, or with ether, and expose it to the air, repeating these operations alternately. The mercury of the thermometer will sink at each exposure, because the volatile liquor, during the evaporation, robs it of its heat. In this way, (especially with the aid of an apparatus, described by M. Cavallo, in the Philosophical Transactions, 1781, p. 509,) water may be frozen, in a thin and small glass ball, by means of ether. The same effect may be obtained, also, by immersing a tube, containing water at the bottom, in a glass of ether, which is to be placed under the receiver of an air pump; or the ether may be allowed to float on the surface of the water. During the exhaustion of the vessel, the ether will evaporate rapidly, and, robbing the water of heat, will completely freeze it; thus exhibiting the singular spectacle of two fluids in contact with each other, one of which is in the act of boiling, and the other of freezing, at the same moment.

Exp.

Dr Marcet's
method of
freezing mer-
cury.

Pl. 3.

By a little modification of the experiment, mercury itself, which requires for congelation a temperature of almost 40° below 0 of Fahrenheit, may be frozen, as was first shown by Dr Marcet. A conical receiver, fig. 54, open at the top, is placed on the plate of an air-pump, and a small tube with a cylindrical bulb at its lower end, containing mercury, is suspended within the receiver, through the aperture, by means of a brass plate, perforated in its centre, and fitting the receiver air-tight, when

laid upon its open neck. The tube passes through this plate, to which it is fitted by a leather adjustment, or simply by a cork secured with sealing wax. The bulb is then wrapped up in a little cotton wool, or, what is better, in a small bag of fine fleecy hosiery, in which a small spirit thermometer graduated below 40° Fahrenheit, may also be included, and after being dipped into sulphuret of carbon or ether* the apparatus is quickly placed under the receiver, which is exhausted as rapidly as possible. In two or three minutes, the temperature sinks to about 45° below 0, at which moment the quicksilver in the stem suddenly descends with great rapidity. If it be desired to exhibit the mercury in a solid state, common tubes may be used, which have originally been about an inch in diameter, but have been flattened by pressure, when softened by the blow-pipe. The experiment succeeds, when the temperature of the room is as high as $+40^{\circ}$ Fahrenheit. H. 126.

159. Immerse a thermometer into an open vessel of water placed over a lamp. The quicksilver rises to 212° , the water then boils, and although the source of heat remains, neither the water nor the steam acquire a higher temperature than 212° ; the heat then becomes latent, and is consumed in the formation of steam.

Latent caloric of aqueous vapours,

To ascertain the absolute loss of thermometric heat in this case, Dr Black instituted the following experiments: he noted the time required to raise a certain quantity of water to its boiling point; he then kept up the same heat till the whole was evaporated, and marked the time consumed by the process; it was thus computed to what height the temperature would have risen, supposing the rise to have gone on above 212° , in the same ratio as below it; and as the temperature of the steam was the same as that of the water, it was fairly inferred that all the heat above 212° was essential to the constitution of aqueous vapour. Dr Black estimated this quantity at about 810° ; that is, the same quantity of heat which is required for the total evaporation of boiling water at 212° would be sufficient to raise the water 810° above its boiling point, or to 1022° had it continued in the liquid state. There are other means of ascertaining the latent heat of steam which lead us to place it between 900° and 1000° . B.

Dr Black's estimate of.

160. The following table of the latent heat of steam and some other vapours is extracted from a paper in the *Philosophical Transactions for 1818*, by Dr Ure.

| | |
|----------------------------------|---------|
| Vapour of Water at 212° | 967°,00 |
| Alcohol | 442°,00 |
| Ether | 302°,38 |
| Petroleum | 177°,87 |
| Oil of Turpentine | 177°,87 |
| Nitric acid | 531°,99 |
| Liquid Ammonia | 837°,28 |
| Vinegar | 875°,00 |

Table of the latent caloric of several fluids by Dr Ure.

* In exhausting a vessel containing either of these fluids, the valves of the air-pump must be metallic.

Latent heat becomes sensible.

161. When steam is again condensed, or when vapours re-assume the liquid state, their latent heat becomes sensible; and in this way it is obvious that a small quantity of steam will, during its condensation, communicate heat sufficient to boil a large quantity of water.

Pl. 2.

The small boiler, represented in fig. 52, taken from Dr HENRY's *Elements of Chemistry*, may be conveniently employed in experiments on the latent heat of steam.

For this purpose the tube *e* must be screwed on the stop-cock *b*, and immersed into the glass of water *f*. The cock *c* being closed, the steam arising from the boiling water *a* will pass into the cold water *f*, the temperature of which will be much augmented by its condensation. Ascertain the increase of temperature and weight, and the result will show how much a given weight of water has had its temperature raised by a certain weight of condensed steam. To another quantity of water, of the same weight and temperature as that in the jar at the outset of the experiment, add a quantity of water at 212° , equal in weight to the condensed steam; it will be found, on comparing the resulting temperatures, that a given weight of steam has produced, by its condensation, a much greater elevation of temperature than the same quantity of boiling water.—H. 1. 129.

Economical use of steam,

Pl. 1.

taken advantage of in some arts.

162. The large quantity of heat, latent in steam renders its application extremely useful for practical purposes. Thus water may be heated, at a considerable distance from the conducting pipe *e* fig. 52. This furnishes us with a commodious method of warming the water of baths, which, in certain cases of disease, it is of importance to have near the patient's bedroom; for the boiler, in which the water is heated, may thus be placed on the ground-floor, or in the cellar of a house; and the steam conveyed by pipes into an upper apartment. Steam may also be applied to the purpose of heating or evaporating water, by a modification of the apparatus.* In breweries and other

* Fig. 52, *g* represents the apparatus for boiling water by the condensation of steam, without adding to its quantity; a circumstance occasionally of considerable importance. The steam is received between the vessel, which contains the water to be heated, and an exterior case; it imparts its caloric to the water, through the substance of the vessel; is thus condensed, and returns to the boiler by the perpendicular pipe. An alteration of the form of the vessel adapts it to evaporation (fig. 52, *h*.) This method of evaporation is admirably suited to the concentration of liquids, that are decomposed, or injured by a higher temperature than that of boiling water, such as medicinal extracts; to the drying of precipitates, &c. In the employment of either of these vessels, it is expedient to surround it with some slow conductor of heat. On a small scale a few folds of woollen cloth are sufficient; and when the vessel is constructed of a large size for practical use, this purpose is served by the brick work in which it is placed. H. 1. 135.

A very convenient apparatus for drying precipitates, &c. by steam is described by Dr Ure. A square tin box, about 18 inches long, 12 broad, and 6 deep, has its bottom hollowed a little by the hammer towards its centre, in which a round hole is cut of 5 or 6 inches diameter. Into this a tin tube, 3 or 4 inches long, is soldered. This tube is made to fit tightly into the mouth of a common tea-kettle, which has a folding handle. The top of the box has a number of circular holes cut into it, of different diameters, into which evaporating capsules are placed. When the kettle, filled with water, and with its nozzle corked is set on a stove, the vapour playing on the bottoms of the capsules, heats them, to any required

manufactories, where large quantities of warm and boiling water are consumed, it is frequently heated by conveying steam into it, or by suffering steam-pipes to traverse the vessels or by employing double vessels, a plan adopted with particular advantage in the preparation of medicinal substances. Where a higher temperature than 212° is required it is necessary to employ steam under adequate pressure.

163. The perfect transparency of steam, and also two other important properties, on which depends its use as a moving power, viz. its elasticity and its condensibility by a reduced temperature, are beautifully shown by a little apparatus contrived by Dr Wollaston. It consists of a glass tube fig. 35, about 6 inches long and $\frac{3}{4}$ inch bore, as cylindrical as possible, and blown out a little at the lower end. It has a wooden handle, to which is attached a brass clip embracing the tube; and within is a piston, which, as well as its rod, is perforated, as shown by the dotted lines. This canal may be occasionally opened or closed by a screw at the top: and the piston rod is kept in the axis of the cylinder by being passed through a piece of cork fixed at the top of the tube. When the instrument is used, a little water is put into the bottom; the piston is then introduced with its aperture left open; and the water is heated over a spirit lamp. The common air is thus expelled from the tube, and when this may be supposed to be effected, the aperture in the rod is closed by the screw. On applying heat, steam is produced, which drives the piston upwards. On immersing the bulb in water, or allowing it to cool spontaneously, a vacuum is produced in the tube, and the piston is forced downwards by the weight of the atmosphere. These appearances may be alternately produced by repeatedly heating and cooling the water in the ball of the instrument. In the original steam engine, the vapour was condensed in the cylinder, as it is in the glass tube; but in the engine as improved by Mr Watt, the steam is pumped into a separate vessel, and there condensed; by which the loss of heat, occasioned by cooling the cylinder every time, is avoided.

Steam is transparent.

Pl. 2.

164. Liquids assume the aëriform state much more rapidly under a diminished pressure, especially if the vapour which is formed be condensed as soon as it is produced, so as to maintain the vacuum; and the cold produced is very great.

Reduction of temperature by evaporation.

On this principle depends Mr Leslie's new and ingenious mode of freezing water, in an atmosphere of any common temperature, by producing a rapid evaporation from the surface of the water itself. The water to be congealed is contained in a shallow vessel, which is supported above another vessel, containing strong sulphuric acid, or dry muriate of lime; or even

Mr Leslie's method of freezing water.

temperature; and being itself continually condensed runs back into the kettle. The orifices not in use may be closed with tin lids. In drying precipitates, the tube of the glass funnel, should be corked up, and the funnel be placed, with its filtre, directly into the proper sized opening. For drying red cabbage, violet petals, &c. a tin tray is provided, which fits close on the top of the box, within the rim which goes about it. The round orifices are left open when this tray is applied. (*Dist. Chem.* 291.)

dried garden mould or parched oatmeal. Any substance, indeed, that powerfully attracts moisture, may be applied to this purpose. The whole is covered by the receiver of an air-pump, which is rapidly exhausted; and as soon as this is effected, crystals of ice begin to shoot in the water, and a considerable quantity of air makes its escape, after which the whole of the water becomes solid. The rarefaction required is to about 100 times; but to support congelation, after it has taken place, 20 or even 10 times are sufficient. The sulphuric acid becomes very warm; and it is remarkable, that, if the vacuum be kept up, the ice itself evaporates. In five or six days, ice of an inch in thickness will entirely disappear. The acid continues to act, till it has absorbed an equal volume of water.

Exp.

Pl. 1.

An elegant manner of making the experiment is to cover the vessel of water (fig. 15, *a*) with a plate of metal or glass, fixed to the end of a sliding wire *b*, which must pass through the neck of the receiver, and be, at the same time, air tight, and capable of being drawn upwards. When the receiver is exhausted, the water will continue fluid, till the cover is removed, when, in less than five minutes, needle-shaped crystals of ice will shoot through it, and the whole will soon become frozen.

In this interesting process, if it were not for the sulphuric acid, an atmosphere of aqueous vapour would fill the receiver; and, pressing on the surface of the water, would prevent the further production of vapour. But the steam, which rises, being condensed the moment it is formed, the evaporation goes on very rapidly, and has no limits but the quantity of the water, and the diminished concentration of the acid.*

Dr Wollaston's Cryophorus.

Pl. 1:

165. It is on the same principle, that the instrument invented by Dr Wollaston, and termed by him the *Cryophorus*, or *Frostbearer*, is founded. It may be formed by taking a glass tube fig. 20, having an internal diameter of about $\frac{1}{8}$ th of an inch, the tube being bent to a right angle at the distance of half an inch from each ball. One of these balls should be about $\frac{1}{3}$ d filled with water, and the other should be as perfect a vacuum as can readily be obtained, the mode of effecting which is well known to those accustomed to blow glass. One of the balls is made to terminate in a capillary tube; and when the water in the other ball has been boiled over a lamp a considerable time, till all the air is expelled, the capillary extremity, through which the steam is still issuing with violence, is held in the flame of the lamp, till the force of the vapour is so far reduced, that the heat of the flame has power to seal it hermetically.

When an instrument of this kind is well prepared, if the empty ball be immersed in a mixture of snow and salt, the water in the other ball, though at the distance of two or three feet, will be frozen solid in the course of a very few minutes. The experiment may be rendered even more striking, if performed according to Dr Marcet's modification of it: the empty ball covered with a little moist flannel, is to be suspended in the

* The most complete account of this new mode of freezing is to be found in the Supplement to the Encycl. Brit. art. *Cold*.

manner shown in fig. 17, within a receiver, over a shallow vessel of strong sulphuric acid, and the receiver is then to be exhausted. In both cases the vapour in the empty ball is condensed by the common operation of cold; and the vacuum produced by this condensation gives opportunity for a fresh quantity to arise from the opposite ball, with a proportional reduction of the temperature of its contents. H. 135.

166. In many natural operations the conversion of water into vapour, and the condensation of vapour in the form of dew and rain, is a process of the utmost importance, and tends considerably to the equalization of temperature over the globe.

Water, as has been seen (158) in passing into vapour from heat, absorbs caloric without increasing in temperature; this vapour ascends in the atmosphere; when the heat diminishes, or when wafted to colder regions, it is condensed, and gives out the caloric it had absorbed. In seasons or situations where the cold becomes still more intense, water is congealed; and in suffering this change it evolves caloric (161) to moderate the progressive reduction of temperature. When warmth is restored, it returns to the liquid state, absorbs caloric, and retards the approaching heat. The transition of seasons is thus moderated; sudden and extreme variations are guarded against, and the temperature of the globe every where preserved more uniform. M. 1. 480.

Temperature
of the globe
how equal-
ized.

167. Until the experiments of Dr Wells* the deposition of dew and hoar frost had been supposed to depend entirely upon the reduction of temperature in the air during the night, and the consequent precipitation of its moisture to the earth. Dr Wells has shown that the deposition of dew and hoar frost, is the consequence of the radiation of caloric from the surface of the earth, and that, under favourable circumstances, the temperature of the ground, especially when its covering is formed of some substance that radiates freely, as grass, is several degrees below that of the atmospheric stratum, a few feet above it. It is this diminished temperature of the earth's surface, that occasions the deposition of dew and hoar frost, which are always observed to be most abundantly formed under a clear unclouded sky; a covering of clouds serves as a mantle to the earth, and prevents the free escape of radiant caloric, hence the advantage of snow and artificial coverings in protecting plants.

Dew and
Hoar frost.

The temperature at which dew begins to be deposited is called the dew point, for determining which a very ingenious instrument has been contrived by Mr Daniell.* A less expensive instrument is made by Mr Pollock of Boston; it is a thermometer filled with ether, having two bulbs at the same extremity of the tube, the upper one being covered with muslin. When sulphuric ether is dropped upon the muslin the temperature of the two bulbs falls, and a deposition of dew becomes visible on the lower and exposed bulb. The degree indicated by the thermometer at that instant is the dew point.

Dew point.

* Essay on Dew, &c.

† Jour. Royal Institut. Vol. 8.

Caloric a fluid.

A vibratory motion.

168. Nothing is known of the nature or cause of heat. It has been by some considered as a peculiar fluid, to which the term *Caloric* has been applied; and many phenomena are in favour of the existence of such a fluid. By others, the phenomena above described have been referred to a *vibratory motion* of the particles of matter, varying in velocity with the perceived intensity of the heat. In fluids and gases the particles are conceived to have a motion round their own axes. *Temperature*, therefore, would increase with the velocity of the vibrations; and increase of *capacity* would be produced by the motion being performed in greater space. The loss of temperature, during the change of solids into liquids and gases, would depend upon loss of *vibratory* motion, in consequence of the acquired *rotatory* motion.

Upon the other hypothesis, *temperature* is referred to the *quantity of caloric* present; and the loss of temperature, which happens when bodies change their state, depends upon the chemical combination of the caloric with the solid in the case of liquefaction, and with the liquid in the case of conversion into the aëriform state. B.

SECTION IV. Of Light.

169. THE minute investigation of those laws of light which relate to its motion, and effects in producing vision, constitutes a branch of the science of Optics, and therefore belongs to Mechanical Philosophy; it is however requisite that some of them should partially be considered as bearing upon important questions of chemical inquiry.

Vision.

The phenomena of vision are produced either by bodies inherently luminous, such as the sun, the fixed stars, and incandescent substances; or they are referable to the *reflection* of light from the surfaces of bodies.

Light transmitted in right lines.

170. The manner in which the eye is affected by luminous bodies shows that light is transmitted in right lines, and every right line drawn from a luminous body to the eye is termed a *ray of light*, and as a congeries of rays possesses the same properties as the single ray, the same abstract term is frequently employed to designate the congeries.

Refraction.

171. Newton first discovered that certain bodies exercise on light a peculiar attractive force. When a ray passes obliquely from air into any transparent liquid or solid surface, it undergoes at entrance an angular flexure, which has been called *refraction*. The refraction is *towards* the perpendicular when the ray passes into a denser medium, and *from* the perpendicular when it passes into a rarer medium. The medium in which the rays of light are caused to approach nearest to the line perpendicular to its surface, is said to have the greatest refractive density.

Refractive power of inflammable bodies.

172. It was found by Newton, that unctuous, or inflammable bodies occasioned a greater deviation in the luminous rays than

their attractive mass, or density gave reason to expect. Hence he conjectured, that both diamond and water contained combustible matter. U. 546.

173. The refractive power of the same inflammable substance bears a proportion to its perfection, insomuch that this property may be used as a test of its purity. Thus Dr Wollaston found that genuine oil of cloves has a refractive power of 1,535, while that of an inferior quality did not exceed 1,498.

May be used as a test of their purity.

174. The density of bodies is not the only circumstance that affects their refractive power; it also depends on their chemical nature, and from the refractive power of bodies we may in many cases infer their chemical constitution.

Refractive power depends on the chemical nature as well as density.

175. The refractive power of compounds is not the mean deduced from that of their components; which, however, it generally is in mere mixtures.

Refractive power of compounds not the mean of that of their constituents,

The following table exhibits the refractive powers of several gaseous and solid bodies; from the experiments of Biot and Arago and from Newton's *Optics*.

| | | | |
|-------------------------------|---------|-----------------------------|---------|
| (Therm. 32° F. Barom. 30 in.) | | | |
| Atmospheric air | 1,00000 | Hydrogen | 6,61436 |
| Carbonic acid | 1,00476 | Muriatic ether, gaseous . . | 1,71344 |
| Nitrogen | 1,03403 | Water | 1,7225 |
| Muriatic acid gas | 1,19625 | Gum arabic | 1,8826 |
| Oxygen | 1,86161 | Alcohol | 2,2223 |
| Carburetted hydrogen . . | 2,09270 | Olive oil | 2,7684 |
| Ammonia | 2,16851 | Diamond | 3,1961 |

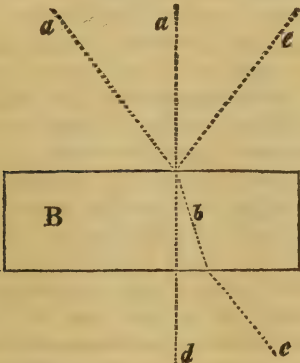
Table of the refractive powers of some bodies.

From this it appears that the combustible gases surpass the others in this property, and that hydrogen gas exceeds them all.

176. When the rays of light arrive at the surfaces of bodies, a part of them, and sometimes nearly the whole, is thrown back, or *reflected*, and the more obliquely the light falls upon the surface, the greater in general is the reflected portion. In these cases the angle of reflection is always equal to the angle of incidence.

Reflected light,

Let *a a* represent pencils of light falling upon the surface of a polished piece of glass *B*, the perpendicular pencil will pass on in a straight line to *d*.



Of the oblique pencil, one portion will enter the glass and suffer refraction towards the perpendicular as *a* at *b*, and re-entering the atmosphere, it will bend from the perpendicular, and re-assume its former direction, as at *c*. Another

portion of the oblique pencil will be reflected at an angle equal to that of its incidence, as at e .

177. When a ray of light passes through an oblique angular crystalline body, it exhibits peculiar phenomena; one portion is refracted in the ordinary way; another suffers extraordinary refraction, in a plane parallel to the diagonal joining the two obtuse angles of the crystal; so that objects seen through the crystal appear double. Transparent rhomboids of carbonate of lime, or Iceland crystal, exhibit this phenomenon of *double refraction* particularly distinct.

Double refraction.

Ordinary and extraordinary refraction,

Refracting power seems dependent upon some position of crystalline particles.

If a ray of light, which has thus suffered double refraction, be received by another crystal, placed parallel to the first, there will be no new division of the rays; but if it be placed in a transverse direction, that part of the ray which before suffered ordinary refraction will now undergo extraordinary refraction, and reciprocally that which underwent extraordinary refraction now suffers ordinary refraction.

If the second crystal be turned gradually round in the same plane, when it has made a quarter of a revolution there will be four divisions of the ray, and they will be reduced to two in the half of the revolution; so that the refracting power appears to depend upon some relation of the position of the crystalline particles.

178. When light is reflected from bodies, it retains, under many circumstances, its former relations to the refractive power of transparent media; but, in certain cases, at angles differing for different substances, the reflected rays exhibit peculiar properties, analogous to those which have suffered extraordinary refraction. Thus, if the flame of a taper reflected at an angle of $52^{\circ} 45'$ from the surface of water, be viewed through a piece of double refracting spar, one of the images will vanish every time that the crystal makes a quarter of a revolution.

Angle of incidence equal to the angle of reflection.

Curious instance of the transmission and reflection of light,

179. When a ray of light is made to fall upon a polished glass surface, at an angle of incidence of $35^{\circ} 25'$, the angle of reflection will be equal to that of incidence. Let us suppose another plate of glass so placed that the reflected ray will fall upon it at the same angle of $35^{\circ} 25'$; this second plate may be turned round its axis without varying the angle which it makes with the ray that falls upon it. A very curious circumstance is observed as this second glass is turned round. Suppose the two planes of reflection to be parallel to each other, in that case the ray of light is reflected from the second glass in the same manner as from the first. Let the second glass be now turned round a quadrant of a circle, so as to make the reflecting planes perpendicular to each other: now, the whole of the ray will pass through the second glass, and none of it will be reflected. Turn the second glass round another quadrant of a circle, so as to make the reflecting planes again parallel, and the ray will again be reflected. When the second glass is turned round, three quadrants, the light will be again transmitted, and none of it reflected. Thus, when the reflecting planes are parallel,

the light is reflected, but when they are perpendicular the light is transmitted. This experiment proves, that, under certain circumstances, light can penetrate through glass when in one position, but not in another. This curious fact was first observed by Malus, who accounted for it by supposing the particles of light to have assumed a particular position as a needle does when under the influence of a magnet, and hence he called this property of light, its *Polarisation*.^{*} It has since been studied with laborious diligence by Dr Brewster, and by M. M. Arago and Biot.[†]

Polarisation
of light.

180. If plates of mica, and certain other crystallized substances, be placed between the glasses employed in the above experiments, so that the reflected rays may traverse them in passing from one surface to the other, it will be found that under certain circumstances, the image of the candle will remain visible; in other words, the light will be *depolarised* in passing through the crystallized medium. Common glass is generally incapable of depolarising the ray, but it acquires the depolarising power when submitted to pressure, or heated, or when it has been heated and very suddenly cooled; the influence of its particles upon those of light becoming then analogous to crystallized bodies.

181. That a sunbeam, in passing through a dense medium, and especially through a triangular prism of glass, gives rise to a series of brilliant tints similar to those of the rainbow, was known in the earliest ages, but it required the sagacity of Newton to develop the cause of the phenomenon. He proved, that light consists of rays differing from each other in their relative refrangibilities; and, guided by their colour considered their number as seven: red, orange, yellow, green, blue, indigo, and violet.[‡] If the prismatic colours, or *spectrum*, be divided into 360 equal parts, the red rays will occupy 45 of these parts, the orange 27, the yellow 48, the green 60, the blue 60, the indigo 40, and the violet 80. Of these rays the red being least refrangible, fall nearest that spot which they would have passed to, had they not been refracted; while the violet rays being most refrangible, are thrown to the greatest distance; the intermediate rays, possess mean degrees of refrangibility.

Prismatic
colours.

182. These differently coloured rays, are not susceptible of further decomposition, by any number of refractions, but when they are collected into a focus they reproduce white light. Upon these phenomena is founded the Newtonian *theory of colours*, which supposes them to depend upon the absorption of all rays, excepting those of the colour observed. Thus green bodies reflect the green rays and absorb the others. All the rays are

Newton's
theory of
colours.

^{*} See Fischer's *Elements of Natural Philosophy*, page 336. Thomson's *System*, 1. p. 16.

[†] *Phil. Trans.* 1813, 1814, 1815, 1816, 1817.—*Annales de Chimie*, tom. 94. *Traite de Physique*.

[‡] Dr Wollaston found, however, that when a beam of light only $\frac{1}{20}$ th of an inch broad is received by the eye, at the distance of ten feet, through a clear prism of flint glass, only four colours are seen viz. red, yellowish green, blue, and violet.

reflected by white bodies, and absorbed by those which are black.

Relative temperature of the prismatic rays.

Calorific, and colorific rays separated by the prism.

Maximum of temperature at the extremity of the red ray.

Concentration of these temperatures.

Light possesses considerable influence over the chemical energies of bodies.

183. If a solar beam be refracted by a prism, and the coloured image received upon a sheet of paper it will be found, on moving the hand gently through it, that there is an evident increase of temperature towards the red ray. This fact seems to have been first noticed by Dr Hutton,* but it is to Dr Herschel† that we are indebted for a full investigation of the subject. If the coloured rays be thrown successively upon delicate thermometers, it will be found, that if the heating power of the violet rays be considered = 16, that of the green rays will be = 26, and of the red = 55. These circumstances suggested the possibility of the heating power of the spectrum extending beyond the red ray; and on applying a thermometer just out of the red ray, and beyond the limits of the visible spectrum, this was found to be the case. A thermometer, in the red ray rose 7° in ten minutes, but just beyond the red ray the rise was = 9° . It is evident, therefore, that, independent of the illuminating rays, there are others which produce increase of temperature, and these from their increase towards the red ray, and from the spot which they principally occupy in the refracted congeries, are possessed of less refrangibility than the visible rays.

Dr Herschel's experiments were repeated, with nearly similar results, by Sir H. Englefield, in 1802, and by Mr Berard, in 1813,‡ who found the maximum of heat to exist just at the extremity of the red ray. Considerable differences in the results of experiments of this kind are, according to Dr Seebeck produced by the particular nature of the medium by which the rays of light are decomposed.§

184. That these calorific rays are susceptible of refraction and reflection, is proved by the intense heat produced when the solar rays are concentrated into a focus by a lens, or by a concave mirror.

185. Light possesses considerable influence over the chemical energies of bodies. If a mixture of equal volumes of the gases called chlorine and hydrogen be exposed in a dark room, they slowly combine, and produce muriatic acid gas; but, if exposed to the direct rays of the sun, the combination is very rapid, and often accompanied by an explosion.

Chlorine and carbonic oxide have scarcely any tendency to combine, even at high temperatures, when light is excluded, but exposed to the solar rays they enter into chemical union. Chlorine has little action upon water, unless exposed to light; and, in that case, the water, which consists of oxygen and hydrogen, is decomposed. The hydrogen unites with the chlorine to produce muriatic acid, and the oxygen is evolved in a gaseous form.

* *Dissertation on Light and Heat*, p. 39.

† *Phil. Trans.* 1800.

‡ *Thomson's Annals*, ii. 163.

§ *Ann. of Phil.* N. S. 8, 235.

186. These, and numerous other similar cases which might be adduced, show that radiant matter influences the chemical energies of bodies, independent of its heating powers. Scheele* was the first who entered upon this curious investigation; and many important facts connected with it have been more lately ascertained by Ritter, Wollaston, and Davy. Scheele threw the prismatic spectrum upon a sheet of paper, moistened with a solution of nitrate of silver, a salt quickly decomposed by the agency of light. In the blue and violet rays the silver was soon reduced, producing a blackness upon the paper, but in the red ray scarcely any similar effect was observed. Wollaston and Ritter discovered that these chemical changes were most rapidly effected in the space which bounds the violet ray, and which is out of the visible spectrum.

Produces
chemical
changes.

187. It has been thus ascertained, that the solar beams are refrangible into three distinct kinds of rays; the *calorific*, or heating rays; the *luminous*, or *colorific*, rays, which produce vision and colour; the *decomposing* rays, or those which have a tendency to interfere with the chemical constitution of bodies.

Division of
solar rays by
refraction.

In the prismatic spectrum these three sets of rays are imperfectly separated, and arranged according to their respective refrangibilities. The heating rays are the least refrangible, the colorific rays are possessed of more refrangibility, and the decomposing, or, as some have called them, the *deoxidizing rays*, are the most refrangible.

Not perfectly
exhibited in
the prismatic
spectrum.

188. Sir H. Davy has observed, that certain metallic oxides, when exposed to the violet extremity of the prismatic spectrum, undergo a change similar to that which would have been produced by exposure to a current of hydrogen; and that, when exposed to the red rays they acquire a tendency to absorb oxygen.† In such general facts, he traces an analogy between the effects of the solar beam, and the agencies of electricity. In the Voltaic circuit, the maximum of heat is at the positive pole, where the power of combining with oxygen is also given to bodies; the agency of rendering bodies inflammable is exerted at the opposite surface; and similar chemical effects are produced by negative electricity, and by the most refrangible rays; and by positive electricity, and the rays which are least refrangible.

Analogy be-
tween the ef-
fect of the so-
lar ray and
that of elec-
tricity.

189. The more refrangible rays of light possess the property of rendering steel or iron magnetic. This property was discovered by Dr Morichini of Rome; but as the experiment did not succeed in other hands, the subject was involved in some degree of uncertainty. The fact, however, has been established by Mrs Somerville of London, who recently gave an account of her researches to the Royal Society. Sewing needles were rendered magnetic by exposure for two hours to the violet ray; and the magnetic property was communicated in a still

The violet
ray of the
spectrum ca-
pable of ex-
citing mag-
netic polarity.

* *Experiments on Air and Fire*, p. 78, &c.

† *Elements of Chemical Philosophy*.

shorter time, when the violet rays were concentrated by a lens. The indigo rays possess the magnetizing power almost to the same extent as the violet; and the blue and green possess the same power, though in a less degree. It is wanting in the orange, yellow and red. Needles were also rendered magnetic by the sun's rays, transmitted through green and blue glass.

Photometer
of Leslie.

190. Professor Leslie has constructed an instrument, called a *Photometer*, on the principle that light, in proportion to its absorption produces heat. It is merely a very delicate and small differential thermometer, enclosed in a thin and pellucid glass tube. One of the bulbs is of black glass, which when the instrument is suddenly exposed to light, becoming warmer than the clear bulb indicates the effect by the depression of the fluid.* From the experiments of Dr Turner and Dr Christison,† this instrument does not appear to be applicable to lights which differ in colour. A differential thermometer containing the vapour of ether, may also, in certain experiments be advantageously used as a *Photometric Thermometer*.‡ § ||

Perfect vegetation requires the influence of solar rays.

191. In nature the influence of the solar rays is very complex, and the growth, colour, flavour, and even the forms of many vegetables, are much dependent upon them. This is seen in many plants which are protected from the sun's rays: celery and endive are thus cultivated with the view of rendering them palatable;¶ and plants which are made to grow in a room imperfectly illuminated, always bend towards the apertures by which the sun's rays enter. The changes too which vegetables effect upon the circumambient atmosphere are influenced by the same cause.

In the animal creation, brilliancy of colour and gaudy plumage belong to the tropical climates; more sombrous tints distinguish the polar inhabitants; and dull colours characterize nocturnal animals, and those who chiefly abide below the surface.

Phosphorescent bodies.

192. There are many substances which, when heated to a certain point, become luminous without undergoing combustion, and such bodies are said to be *phosphorescent*. The temperatures which they require for this purpose are various; it generally commences at about 400°, and may be said to terminate at the lowest visible redness. Some varieties of phosphate of lime, of fluor spar, of bituminous carbonate of lime, of marble, and sand, and certain salts, are the most remarkable bodies of this description.** Their luminous property may be best exhibited by scattering them in coarse powder upon an iron plate heated nearly to redness. Oil, wax, spermaceti, and butter, when nearly boiling, are also luminous.

* Leslie on *Heat*, p. 424.

† Edin. *Philos. Jour.* xiii. 4.

‡ Brande, *Phil. Trans.* 1820.

§ A new photometer has been described by Mr Ritchie. See *Quarterly Journal*, Vol. 19, p. 299.

|| For a description of Count Rumford's Photometer, see *Philos. Trans.* Vol. 84.

¶ The process is termed *etiolation* or blanching

** Wedgwood, *Phil. Trans.* Vol. 82.

193. Another class of phosphorescent bodies have been termed *solar phosphori*, from becoming luminous when removed into a dark room after having been exposed to the sunshine.* Of this description are Canton's, Baldwin's, and the Bolognian phosphorus. Canton's phosphorus is prepared thus:—Calcine oyster-shells in the open fire for half an hour, then select the whitest and largest pieces and mix them with one third their weight of flowers of sulphur, pack the mixture closely into a covered crucible, and heat it to redness for an hour. When the whole has cooled, select the whitest pieces for use.†

Solar Phosphori.

Canton's compound.

Baldwin's phosphorus is prepared by heating nitrate of lime to a dull red heat, so as to form it into a compact mass: and the Bolognian phosphorus, discovered by Vincenzo Cascariolo, a shoemaker of Bologna, is made by reducing compact sulphate of baryta to a fine powder, which is formed into cakes with mucilage, and these are heated to redness.‡

Baldwin's and the Bolognian phosphorus.

194. Mr B. Wilson has also made a variety of curious experiments on solar phosphori; and, he has discovered the simplest and most effectual of these bodies, which may be obtained by closely observing the following directions:—Take the most flaming coals off a brisk fire, and throw in some thick oyster-shells; then replace the coals, and calcine them for an hour; remove them carefully, and, when cold, it will be found that after exposing them for a few minutes to the light, they will glow in the dark, with most of the prismatic colours.§

Wilson's experiments.

195. A third set of bodies, belonging to this class, are those which are *spontaneously phosphorescent*. Such are especially, the flesh of salt-water fish just before it putrefies, and decayed wood. The *glow-worm*, and the *lantern-fly*, are also luminous when alive; and the *hundred legged worm*, and some others, shine brilliantly when irritated.||

Spontaneous Phosphori.

It appears from the experiments of Canton and of Dr Hulme,* that sea-fish become luminous in about twelve hours after death, that it increases till putrefaction is evident, and that it then decreases. Immersion in sea-water does not affect this luminous matter, on the contrary, the brine is itself rendered luminous; but it is extinguished by pure water, and by a variety of substances which act chemically upon the animal matter.

196. Percussion and friction are often attended by the evolution of light as when flint pebbles, pieces of sugar, and other substances, are struck or rubbed together. The crystallization of some substances as benzoic acid, and acetate of potassa has been found to be attended with similar phenomena.**

Light from percussion or friction.

197. From experiments in which air has been intensely heated, it has been concluded that gaseous matter is incapable

Gases incapable of becoming luminous.

* For practical directions for observing the phosphorescence of bodies, see Faraday's *Chemical Manipulation*.

† *Phil. Trans.* Vol. 58.

§ Wilson on *Phosphori*, p. 20.

¶ *Phil. Trans.* Vols. lix. xc. and xci.

‡ Aikin's *Dictionary*, Art. *Phosphori*.

|| See *Bost. Jour.* 2. 101.

** Brewster's *Journal*, 3. 368.

of becoming luminous ; for, though the temperature of air be such as to render solid bodies white hot, it does not itself become visible.* Flame, however, may, in general, be regarded as luminous gaseous matter. Hydrogen gas, probably, furnishes the purest form of flame which can be exhibited ; for the flames of bodies which emit much light, derive that power from solid matter which is intensely ignited and diffused through them, and which, in ordinary flames, as of gas, tallow, wax, oil, &c. consists of finely divided charcoal.

Height and
temperature
of flame.

199. The intensity of the heat of flames which are but little luminous, as of hydrogen gas, spirit of wine, &c. may be shown by introducing into them some fine platinum wire, which is instantly rendered white hot in those parts where the combustion is most perfect. It is even intensely ignited in the current of air above the flame, as may be shown by holding a piece of platinum wire over the chimney of an Argand lamp fed with spirit of wine ; the high temperature of this current is also exhibited by the common expedient of lighting paper by holding it in the heated air which rushes out of a common lamp-glass.

The high temperature of flame is further proved by certain cases of combustion without flame. Thus, if a heated wire of platinum be introduced into any inflammable or explosive mixture, it will become *ignited*, and continue so till the gas is consumed ; but *inflammation* will, in most cases, only take place when the wire becomes white hot.

Exp. This experiment is easily made by pouring a small quantity of ether into the bottom of a beer-glass, and holding a piece of heated platinum wire a little above its surface ; the wire becomes red hot, but does not inflame the vapour of the ether till it acquires an intense white heat.

Pl. 2. The same fact is exhibited by putting a small coil of platinum wire round the wick of a spirit lamp, fig. 34, which, when heated, becomes red hot, and continues so, as long as the vapour of the spirit is supplied, the heat never becoming sufficiently intense to produce its inflammation.

Platinum
wire lamp.

200. Such being the nature of flame, it is obvious, that if we *cool* it by any means, we must at the same time *extinguish* it. This may be effected by causing it to pass through fine wire gauze, which is an excellent conductor and radiator of heat, and consequently possessed of great cooling power.

Exp. If a piece of fine brass or iron wire-gauze be brought down upon the flame of a candle, or what answers better, upon an inflamed jet of oil gas, it will, as it were, cut the flame in half. That the cool gaseous matter passes through, may be shown by again lighting it upon the upper surface.

Effect of
wire-gauze
on flame.

The power, therefore, of a metallic tissue thus to extinguish flame, will depend upon the heat required to produce the combustion, as compared with that acquired by the tissue ; and the flame of the most inflammable substances, and of those that produce most heat in combustion, will pass through a metallic tissue that will interrupt the flame of less inflammable substances,

* Wedgwood, *Phil. Trans.* 1792.

or those that produce little heat in combustion ; so that different flames will pass through at different degrees of temperature.

201. The discovery of these facts, respecting the nature and properties of flame, led Sir H. Davy to apply them to the construction of the *Miners' safety lamp*, which will be explained under the article *Carburetted hydrogen gas*. Davy's safety lamp.

202. The phenomena exhibited by phosphorescent and incandescent bodies, and in the process of combustion, have sometimes been explained upon the idea that the light and heat evolved, were previously in combination with the substances, and that they are afterwards merely emitted, in consequence of decomposition ; and that the solar phosphori absorb light and again give it out unchanged. Mr Brande and others consider it more probable that any particles violently repelled into space may become *radiant matter*, than that it should consist of a *specific* substance : thus mechanical action, and chemical changes, may each tend to the emission of radiant matter ; and incandescence will result when the vibrations which heat occasions among the particles of bodies are of such violence as to cause their repulsion into space.* On the properties of phosphorescence and incandescence.

SECTION V. Electricity.

203. THE term *electricity* is derived from the Greek word *ἤλεκτρον*, *amber*, on account of the property which this substance was known to possess of attracting light substances when rubbed. If a piece of sealing-wax and of dry warm flannel be rubbed against each other, they both become capable of attracting and repelling light bodies. A dry and warm sheet of paper, rubbed with India rubber, or woollen, or a tube of glass rubbed upon silk, exhibit the same phenomena. In these cases the bodies are said to be *electrically excited* ; and when in a dark room, they always appear luminous. Electrical excitement.

204. If two pith-balls be electrified by touching them with the sealing-wax or with the flannel, they repel each other ; but if one pith-ball be electrified by the wax, and the other by the flannel, they attract each other. The same applies to the glass and silk : it shows a difference in the electricities of the different bodies, and the experiment leads to the conclusion, that *bodies similarly electrified repel each other, but that when dissimilarly electrified they attract each other*. Repulsion and attraction.

The term *electrical repulsion* is here used merely to denote the appearance of the phenomenon, the separation being probably referable to the new attractive power which they acquire, when electrified, for the air and other surrounding bodies. Repulsion.

* See Davy's *Elements*, 1. 213, &c.—Murray's *System*, 1. 570—Ure's *Dictionary*, article *Caloric*—Hare in *Amer. Jour.* vol. 4. 12, &c.

If one ball be electrified by sealing-wax rubbed by flannel, and another by silk rubbed with glass, those balls will repel each other ; which proves that the electricity of the silk is the same as that of the sealing-wax. But if one ball be electrified by the sealing-wax and the other by the glass, they then attract each other, showing that they are oppositely electrified.

Dufay's
theory.

205. The terms *vitreous* and *resinous* electricity were applied to these two phenomena. According to Dufay the vitreous and resinous electricities are distinct ; an unexcited body contains both in a state of combination or neutralization, and cannot, therefore, exhibit any electrical attractions or repulsions. But friction disturbs this combination, or electric equilibrium, causing the vitreous electricity to accumulate in one body and the resinous in the other. They are both consequently in an excited state, and continue to be so till each recovers that kind of electricity which it had lost.

Franklin's
theory.

A different explanation was proposed by Dr Franklin, which is founded on the supposition that there is only one kind of electricity. When bodies contain their natural quantity of electricity, they do not manifest any electrical phenomena ; but they are excited either by an increase or diminution in that quantity. Thus on rubbing a piece of glass with a woollen cloth, the electrical condition of both substances is disturbed ; the former acquires more, the other less than its natural quantity. These different states are expressed by the terms *plus* and *minus* or *positive* and *negative*, the first corresponding to the vitreous, the second to the resinous electricity of Dufay.*

206. The substances enumerated in the following table become positively electrified when rubbed with those which follow them in the list, but with those which precede them they become negatively electrical.†

| | |
|-----------------|--------------|
| Cat's skin. | Paper. |
| Polished glass. | Silk. |
| Woollen cloth. | Gum lac. |
| Feathers. | Rough glass. |



Electrometer.

207. Very delicate pith-balls, or strips of gold leaf, are usually employed in ascertaining the presence of electricity ; and, by the way in which their divergence is affected by glass or sealing-wax, the kind or state of electricity is judged of. When properly suspended or mounted for delicate experiments, they form an *electrometer* or *electroscope*. For this purpose the slips of gold leaf are suspended by a brass cap and wire in a glass cylinder ; they hang in contact when unelectrified ; but when electrified they diverge.

Method of determining the kind of electricity.

208. The kind of electricity by which the gold leaves are diverged may be judged of by approaching the cap of the instrument with a stick of excited sealing-wax ; if it be *negative*

* As writers on chemistry continue to use the terms *positive* and *negative*, they are here retained.

† Biot, *Traité de Physique*, tom. ii. p. 220.

the divergence will increase ; if *positive*, the leaves will collapse, upon the principle of the mutual annihilation of the opposite electricities, or that bodies similarly electrified repel each other, but that when dissimilarly electrified they become mutually attractive. (204.)

209. Some bodies suffer electricity to pass readily along their surfaces, and are called *conductors*. Others only receive it upon the spot touched, and are called imperfect or *nonconductors*. They are also called *insulators*.* The metals are all conductors ; dry air, glass, sulphur, and resins, are nonconductors. Water, damp wood, spirit of wine, damp air, and some oils, are imperfect conductors.

Conductors and nonconductors.

210. Rarefied air admits of the passage of electricity ; so does the Torricellian vacuum.

Electricity passes thro' rarefied air or a vacuum.

211. There appears to be no constant relation between the state of bodies and their conducting powers : among solids, metals are conductors, but gums and resins are nonconductors ; among liquids, strong alkaline, acid, and saline solutions, are good conductors ; pure water is an imperfect conductor, and oils are nonconductors ; solid wax is almost a nonconductor, but when melted, a good one. Conducting powers belong to bodies in the most opposite states ; thus the flame of alcohol, and ice, are equally good conductors.† Glass is a nonconductor when cold, but conducts when red-hot ; the diamond is a nonconductor, but pure and well-burned charcoal is among the best conductors.

No constant relation between the state of bodies and their conducting powers.

212. There are many mineral substances which show signs of electricity when heated, as the tourmalin, topaz, diamond, boracite, &c. ; and in these bodies the different surfaces exhibit different electrical states.‡

Some substances become electric by being heated.

213. When an electrical machine is in good order, and the atmosphere dry, it produces a crackling noise when the plate or cylinder is turned, and flashes or sparks of light are seen upon various parts of the glass passing from the cushion to the conductor : if the knuckle be held near the conductor, sparks pass to it through some inches of air, with a peculiar noise, and excite slightly painful sensation in the part upon which they are received. It is conjectured that the cause of the light thus perceived, is the sudden compression of the air or medium through which the electricity passes, and it is always probably attended by a proportionate elevation of temperature, as is shown by the power of the spark to inflame spirit of wine, fulminating silver, and other easily inflammable compounds.

Phenomena observed in using electrical machines.

Light and Heat.

* The *insulation* of substances is frequently required in electro-chemical experiments ; a plate of mica is the best substance for the purpose, then a plate of resin or wax, or in their absence, a plate of warm glass. *Faraday*.

† Biot, *Traité de Physique*, tom. ii. p. 213.

‡ For a description of Electrical machines and a more full account of Electricity, see *Cambridge Natural Philosophy*, vol. 2, and Fischer's *Elements of Nat. Philos.* p 104.

Electricity
by induction.

214. Another cause of excitement is proximity to an electrified body, which has a tendency to *induce* an electrical state opposite to its own. Thus an excited stick of sealing-wax attracts light bodies in its vicinity, because, being itself negative, it occasions them to be positively electrified. If an insulated conductor be electrified, and an uninsulated conductor be opposed to it, there being between the two a thin stratum of air, glass, or other nonconductor, the uninsulated conductor, under such circumstances, acquires an opposite electrical state to that of the originally electrified insulated conductor. In this case, the uninsulated body is electrified by *induction*, and the induced electricity remains evident, until an explosion, spark, or discharge happens, when the opposite electricities annihilate each other. Induced electricity may thus be exhibited through a long series of insulated conductors, provided the last of the series be communicated with the earth.

Pl. 2.

Illustration.

Thus, in fig. 37, *A*, may represent the positive conductor of the electrical machine; *b*, *c*, and *d*, three insulated conductors, placed at a little distance from each other, *d* having a chain touching the ground; then the balls 1, being positive, will attract the balls 2, which are rendered negative by induction. Under these circumstances, each of the conductors becomes polar, and the balls 3 are positive, while 4 are negative, 5 positive, 6 negative, &c.: the central points of the conductors, *b c d*, are neutral. When these opposite electrical states have arrived at a certain intensity, sparks pass between the different conductors, and the electrical phenomena cease.

Leyden
phial.

215. Upon the principle of induction it is, that the accumulation of electricity in the *Leyden phial* is effected. It consists of a thin glass jar, coated internally and externally with tin foil to within a short distance of its mouth. When the inner surface is rendered positive by union with the conductor of the electrical machine, the exterior, being connected with the ground, becomes negative by induction. When the inner and outer surfaces are united by a conductor, all electrical accumulation is annihilated by a powerful spark, and the two opposite states are found to have been precisely equivalent.

If the communication between the opposite surfaces of the Leyden phial be made by the hands, a painful jarring sensation is felt at the joints of the fingers, the elbows, shoulders, and chest, commonly called the *electrical shock*.

Connection of
Leyden jars.

216. If one Leyden jar be insulated with its internal surface connected with the positive conductor, another jar may be charged from its exterior coating; and if this second jar be insulated, a third may be charged from its exterior coating, and so on for any number of jars, provided always that the exterior coating of the last jar be connected with the ground. In this case, a polar arrangement, similar to that of the conductors just described, (214) will have been formed, glass being the medium of induction instead of air.

Illustration.

Pl. 2.

Let *P*, fig. 42, be the positive conductor of the electrical machine, and *a b c* three insulated Leyden phials, the outer coating of *c* being connected with the ground; it is then obvious, that there will be the same polar state as in the

conductors just noticed ; that the insides of *a*, *b*, and *c*, will be positive, and the outsides negative ; and that, consequently, on removing the jars from each other, they will all be similarly charged, and that if the three inner surfaces *p p p* and the outer surfaces *n n n* be united, the whole may be discharged as one jar.

217. The operation of the instrument called the *Electrophorus* (or bearer of electricity) is referable to the phenomena of induction.

The *electrophorus*, fig. 41, consists of two metallic plates, *a a*, with an intervening plate of resinous matter, *b*, for which equal parts of shellac, resin, and Venice turpentine, are generally used, the mixture being carefully melted in a pipkin, and poured, whilst liquid, into a wooden or metal hoop, of a proper size, placed upon a polished surface of glass or marble, from which it easily separates when cold ; it should be about half an inch thick, and the smooth surface being uppermost the lower side should be covered with tin foil, or attached to any other metallic plate ; a polished brass plate, with a glass handle *c* attached to it, is then placed upon the upper surface of the resinous plate, and of rather smaller diameter. The resin is then to be excited with a piece of dry fur, and the instrument will be found to exhibit the following phenomena :

Upon raising the brass plate by its insulating handle, it will be found very feebly electrical ; replace it, touch it with the finger and again lift it off by its handle, and it will give a spark of positive electricity. This process may very often be repeated without fresh excitation, which circumstance, as well as the nature of the electrical charge, shows that the electricity of the moveable brass plate is not directly derived from the resin, but that it depends upon induction.*

The *electrophorus* may often be used for the same purpose as the electrical machine, and in the laboratory it furnishes a very convenient substitute for that more expensive piece of apparatus.

218. Electricians generally employ the term *quantity* to indicate the absolute quantity of electric power in any body, and the term *intensity* to signify its power of passing through a certain stratum of air or other ill-conducting medium.

If we suppose a charged Leyden phial to furnish a spark, when discharged, of one inch in length, we should find that another uncharged Leyden phial, the inner and outer coating of which were communicated with those of the former, would upon the same quantity of electricity being thrown in, reduce the length of the spark to half an inch ; here, the *quantity* of electricity remaining the same, its *intensity* is diminished by one-half, by its distribution over the larger surface.

219. The power of the Leyden jar is proportioned to its surface, but a very large jar is inconvenient and difficult to procure ;

Pl. 2.

Electrophorus.

Mode of using it.

The electrophorus used as an electric machine.

Quantity and intensity of electric power.

Illustration.

Power of the Leyden jar in proportion to its surface.

* The most ample directions for constructing this useful instrument, and for applying electricity in the laboratory, will be found in Faraday's *Chemical Manipulation*, p. 436.

Electrical
Battery.

Its discharge
attended with
report, can
prove fatal to
animal life.

Produces
combustion,
&c.

Other sources
of electricity.

the same end is attained by arranging several jars, so that by a communication existing between all their interior coatings, their exterior being also united, they may be charged and discharged as one jar. Such a combination is called an electrical *Battery*, and is useful for exhibiting the effect of accumulated electricity.

The discharge of the battery is attended by a considerable report, and if it be passed through small animals it instantly kills them; if through fine metallic wires, they are ignited, melted, and burned; and gunpowder, cotton sprinkled with powdered resin, and a variety of other combustibles, may be inflamed by the same means.

220. There are many other sources of electricity than those just noticed. When glass is rubbed by mercury, it becomes electrified, and this is the cause of the luminous appearance observed when a barometer is agitated in a dark room, in which case flashes of light are seen to traverse the empty part of the tube. Even the friction of air upon glass is attended by electrical excitation: for Mr Wilson found that by blowing upon a dry plate of glass with a pair of bellows, it acquired positive electricity. Whenever bodies change their forms, their electrical states are also altered. Thus during the congelation of melted resins and sulphur, electricity is rendered sensible. It is also developed during various natural processes; as evaporation and the condensation of vapour, which may aid in accounting for certain electrical phenomena of the atmosphere.

Exp.

Place a small iron cup, heated nearly to redness, over an electrometer, on dropping into it a small portion of water vapour will be produced, and the leaves of the electrometer will diverge.

Electricity
from the con-
tact of metals.

221. Electricity is excited by the *contact* of different conducting bodies with each other, especially when two dissimilar metals are employed. When a plate of zinc furnished with a glass handle is brought into contact with one of copper or silver, it is found, after removal, to be positively electrical, and the silver or copper is left in the opposite state. It has even been found that two discs of the same metal, heated to different temperatures, give similar results.

Galvanism.

The electricity thus developed was distinguished as Galvanism, from the circumstance that Galvani, an Italian physiologist, about the year 1789, observed the first striking phenomenon which led to the discovery. He observed it only in its power of affecting the animal system. It was found that if the nerve of a recently killed frog was attached to a silver probe, and a piece of zinc was brought into contact with the muscles of the animal, violent contractions would be produced at every contact of the metals. Exactly the same effect is produced by an electric spark, or the discharge of a small Leyden phial.

The following experiment produces a similar effect.

Exp.

Place a piece of zinc upon the tongue, and a piece of silver under it, whenever the projecting edges of these different metals are made to touch a peculiar

taste or sensation will be perceived, and if the pieces are large the contact will sometimes be accompanied by a flash of light.*

222. From these and similar experiments Galvani concluded that the phenomena were owing to the communication of electricity generated by the animal system. Volta supposed that the electricity was derived from the action exerted between the metal and the moist animal fibre, and soon discovered that it is evolved by arrangements wholly unconnected with any process of vitality. His discovery of a method of augmenting the galvanic energy and of thus enabling us to investigate its effects with more precision, has acquired for this form of electricity the epithet *Voltaic*. Galvani's hypothesis.
Volta's.

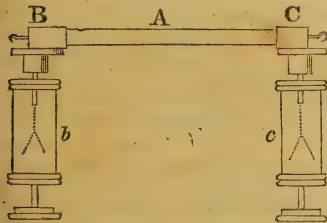
223. When dissimilar metals are brought into contact in the manner just stated (100) the most oxidable metal is always positive, in relation to the least oxidable metal, which is negative; and the more opposite the metals in these respects, the greater the electrical excitation. If the metals be placed in the following order, each will become positive by the contact of that which precedes it, and negative by the contact of that which follows it; and the greatest effect will result from the contact of the most distant metals.

- Platinum.
- Gold.
- Silver.
- Mercury.
- Copper.
- Iron.
- Tin.
- Lead.
- Zinc

224. In these cases the chemical properties of the metals are observed to be affected. If a silver and a zinc wire be put into a wine glass full of dilute sulphuric acid, the zinc wire only will evolve gas; but upon bringing the two wires in contact with each other, the silver will also copiously produce air bubbles. Chemical action accompanying that of electricity.

225. If a number of alternations be made of copper or silver leaf, zinc leaf, and thin paper, the electricity excited by the Electric column.

contact of the metals will be rendered evident to the common electrometer. A, represents a glass tube, in which are regularly arranged a number of alternating plates of silver, zinc and thin paper. The metallic cap B is in contact with the silver plate and C with the zinc plate, at the respective extremities of the tube. Upon examining the electrometers, it will be found that *b* is negatively diverged and *c* positively.



* Advantage may be taken of this for ascertaining whether a substance be a conductor of electricity or not, by placing the substance between the two metals before making the contact. All the pure metallic bodies, and all combinations of them with each other, conduct electricity so well as to occasion taste. See Faraday's *Chem. Manip.* 402.

Pl. 2.

226. If the same arrangement be made with paper or cloth moistened with brine, or a weak acid, fig. 38, it will be found on bringing a wire communicating with the last copper plate into contact with the first zinc plate, that a spark is perceptible, and also a slight shock, provided the number of alternations be sufficiently numerous. This is the *VOLTAIC* apparatus.

Volta's.

Another mode of constructing the apparatus.

227. Several modes of constructing this apparatus have been adopted, with a view to render it more convenient or active. Sometimes double plates of copper and zinc soldered together, are cemented into wooden troughs in regular order, fig. 48, the intervening cells being filled with water, or saline or acid solutions.

Coronne de tasse another variety of form.

228. Another form consists in arranging a row of glasses, containing dilute sulphuric acid, in each of which is placed a wire or plate of silver or copper *c*, and one of zinc *z*, not touching each other, but so connected by metallic wires, that the zinc of the first cup may communicate with the copper of the second; the zinc of the second with the copper of the third, and so on throughout the series, as represented in fig. 44.

By dipping the fingers into the extreme cups a shock will be felt; and on making a communication between them by a wire, it will be found that the copper plates instantly acquire the power of decomposing the dilute sulphuric acid, and that the chemical action of the zinc is much augmented. One advantage of this arrangement over the former (227) is, that both surfaces of the metal are exposed; whereas in the other, by soldering the plates together, its action is diminished.

Pl. 3.

229. In fig. 55, the trough *A* is made of earthenware, with partitions of the same material, and the metallic plates are attached to a bar of wood, so that they can be immersed and removed at one operation. The troughs are filled with dilute acid,* and by uniting them in regular order, the apparatus may

Troughs.

* A mixture of proper strength for galvanic batteries is obtained by adding two parts in bulk of oil of vitriol and one part of common nitric acid to 100 parts of water, the whole being well stirred until mixed. Its power should in all cases be ascertained before it is poured into the trough, by dipping a piece of clean zinc into a little of it in a glass and observing the degree of action exerted upon the metal. A stream of bubbles should be disengaged so small that their size can hardly be distinguished by the naked eye, and which, as they rise up through the fluid, should be carried freely in different directions by the currents in the fluid itself. If the action be so strong as to evolve bubbles of a considerable size and in rapid succession, the acid must be diluted. If, little or no action can be perceived, acid must be added.

The cells of the trough are to be filled to within half an inch of their upper edges; when the plates are in their places the mixture should not flow from one cell into another.

When two or more troughs are to be connected, the arrangement should first be examined to ascertain that the plates of both troughs are in the same relative position and order; when that is the case they may be connected, and considered but as one trough. The connexion should be made by wide strips of copper or lead, and they should not merely enter the two cells containing the plates to be connected, but should be brought into firm and close contact with the plates, so that a good metallic communication may exist between them.

Whenever a junction is to be made in the wires coming from the poles of a battery, it should be effected by a sound metallic soldering or brazing. If the junction is to be only temporary, it is effected by bringing the clean surfaces into contact and retaining them so by pressure or otherwise. Wires may be twisted together, their surfaces being first well cleaned and brightened, or if they are stiff and rigid

be enlarged to any extent. It is thus that the great apparatus of the Royal Institution is constructed.

230. When from 500 to 1000 double plates are thus arranged and rendered active by immersion into a liquid consisting of about sixty parts of water with one of nitric and one of sulphuric acid, very brilliant effects are produced when the opposite poles are properly united by conductors. Thus, if a piece of charcoal united with the negative wire be made to touch another piece united with the positive wire, a bright spark and intense ignition ensue, and by slowly withdrawing the points from each other a constant current of electricity takes place through the heated air, producing a magnificent arc of intense light.

231. When the metals and other inflammable bodies are placed in this arc of fire they burn with great brilliancy, and those which are most difficult of fusion give evidence of the intensity of the heat by instantly melting; and some earthy and other bodies, infusible by ordinary methods, are liquefied by the same means. The shock is painful and dangerous. When the communication between the points of charcoal is made in rarefied air, the annihilation of the opposite electricities takes place at some inches distance, producing a stream of deep purple light.

Galvanic combustion of charcoal.

Combustion and fusion of metals.

232. When the poles of the Voltaic apparatus are connected by a steel wire, it acquires magnetic properties; and if by a platinum or other metallic wire, that wire exhibits numerous magnetic poles, which attract and repel the common magnetic needle. This very curious fact was first observed by Professor Oersted, of Copenhagen.*

Magnetism resulting from galvanism.

233. On immersing the wires from the extremes of this apparatus into water, it is found that the fluid suffers decomposition, and that oxygen gas is liberated at the positive wire or pole, and hydrogen gas at the negative pole.

Decomposition of water

234. One of the first discoveries of the chemical agency of the pile was its power of decomposing water. Two pieces of any metallic wires are thrust through separate corks, which are fitted into the open ends of a glass tube in such a way, that the

Exp.

they should be first slightly twisted together, and then bound round by twenty or more turns of clean copper wire of smaller size. Either in twisting or in binding wires, two or three loose turns must never be considered as sufficient, but the two pieces must be so twisted or bound together, as to have the steadiness of one piece.

When a junction is to be made and broken again frequently, as happens in many experiments, it should be done at one place only in the metallic communication; the points of contact should be perfectly clean and the contact insured by firm pressure.

It is often useful to amalgamate the surfaces of the ends, or places of contact, of the wires, for then, if they be moistened with a little mercury, the fluid metal causes a perfect contact, the moment they are connected together. Clean copper wires are readily amalgamated by washing them with a solution of nitrate of mercury, then washing them in water and afterwards dipping them in mercury. The amalgamated surfaces will be less liable to oxidate and become foul, if a little tallow and metallic mercury be well rubbed on them by means of leather. A cup of mercury forms a convenient metallic communication into which the amalgamated wires may be dipped.—Faraday's *Chemical Manipulation*, Sect. xvii.

* For a full account of Electro-magnetism, see *Camb. Nat. Philos.* Vol. 2d.

Pl. 2.

extremities of the wires when the corks are in their places, may not be in contact, but may be at the distance from each other of about a quarter of an inch (see fig. 46, *a*.) If the parts of the wire which project from without the tube, be made to communicate, the one with the zinc or positive end, and the other with the copper or negative end, of a galvanic battery, a remarkable appearance takes place. The wire, connected with the zinc or positive end of the pile or trough, where it is in contact with the water, if of an oxidable metal, is rapidly oxidized; while, from the negative wire a stream of small bubbles of gas arises (232.) But if the wires employed be of a metal which is not susceptible of oxidation, such as gold or platinum, gas is then extricated from both wires, and, by a simple contrivance, may be separately collected. An apparatus for this purpose is shown by fig. 51, where the wires *p* and *n*, instead of being introduced into a straight tube, are inclosed in a syphon, and terminate before they reach the end, in which a small hole is to be ground. When a stream of voltaic electricity is made to act upon water thus confined, oxygen gas is found, at the close of the experiment, in the leg connected with the positive end of the battery and hydrogen gas in that connected with the negative end; and in the proportions, which, by their union, compose water. At an early period of the inquiry, it was found, however, by Mr Cruickshank, that the water surrounding the positive wire became impregnated with a little acid; and that around the negative wire with a little alkali. If, instead of water, we employ a metallic solution, the metal is revived round the negative wire *n*, and no hydrogen gas is liberated.

Method of obtaining oxygen and hydrogen separately.

Pl. 2.

Exp.

235. The gases constituting water, it was afterwards discovered by Sir H. Davy, may be separately produced from two quantities of water not immediately in contact with each other. The fact is of peculiar importance from its resemblance to other more recent ones, which have led that distinguished philosopher to the discovery of the general laws of electro-chemical action. Two glass tubes, (*p* and *n*, fig. 45,) about one-third of an inch in diameter and four inches long, having each a piece of gold wire sealed hermetically into one end and the other end open, were filled with distilled water, and placed, inverted in separate glasses, filled, also, with that fluid. The two glasses, *a* and *b*, were made to communicate, either by dipping the fingers of the right hand into one glass, and those of the left into the other, or by interposing fresh animal muscle, or a living vegetable, or even moistened thread, as shown at *c*. The gold wires, projecting from the sealed ends of these tubes, were then connected, the one with the positive, the other with the negative end of the trough. Gas was immediately evolved from both wires. At the close of the experiment, in the tube *p*, oxygen gas was found; in the negative tube *n*, hydrogen. The proportions by measure were, as nearly as possible, those which result from the decomposition of water, *viz.* two of hydrogen to one of oxygen

gas. Now if these gases arose, as they necessarily must, from the decomposition of the same portion of water, that portion of water must have been contained either in the tube *p* or in the tube *n*. In the former case, the hydrogen gas, found after the process in *n*. must have passed invisibly from *p* to *n*, through the intermediate substance *c*. Or, if the water was decomposed in *n*, then the reverse process must have happened with respect to the oxygen; and it must have been transmitted, in a like imperceptible manner, from *n* to *p*. Facts of this kind, evincing the transference of the elements of a combination, to a considerable distance, through intervening substances, and in a form that escapes the cognizance of our senses, however astonishing, it will appear from the sequel, are sufficiently numerous and well established. It appears, also, from the experiments of Mr Porrett, that water may be forced, contrary to its gravity, through the compact substance of a bladder, from the positive to the negative wire of a galvanic battery, composed of plates only $1\frac{1}{4}$ inch square. H. 1. 177.

236. All other substances are decomposed with similar phenomena, the inflammable element being disengaged at the negatively electrical surface; hence it would appear, upon the principle of similarly electrified bodies repelling each other, and dissimilarly electrified bodies attracting each other, (204) that the inherent or natural electrical state of the inflammable substances is *positive*, for they are attracted by the negative or oppositely electrified pole; while the bodies, sometimes called supporters of combustion, or acidifying principles, are attracted by the positive pole, and, therefore, may be considered as possessed of the *negative* power.

Combustible constituents, join in the negative pole.

Explanation:

237. When bodies are thus under the influence of electrical decomposition, their usual chemical energies are suspended, and some very curious phenomena are observed, which may be illustrated by the following experiments.

Chemical union destroyed by galvanism.

Fill the glass tubes *a a*, fig. 40, which are closed at top and open at bottom, with infusion of violets, or red cabbage, and invert them in the basins *b b*, containing a solution of Glauber's salt, and connected by the glass tube *c*, also containing the blue infusion; *p* and *n* are platinum wires, which pass into the tubes nearly to the bottom, and which are to be connected with the positive and negative extremities of the Voltaic apparatus. It will be found that oxygen is evolved at the wire *p*, and hydrogen at *n*, derived from the decomposition of the water. The Glauber's salt, which consists of sulphuric acid and soda, will also be decomposed; and the blue liquor will be rendered red in the positive vessel, by the accumulation of sulphuric acid, and green in the negative, by the soda, while the acid and alkali will each traverse the tube *c* without uniting, in consequence of being under the influence of electrical attraction.

Pl. 2.
Exp.

238. The most difficultly decomposable compounds may be thus resolved into their component parts by the electrical

agency ; by a weak power the proximate elements are separated, and by a stronger power these are resolved into their ultimate constituents.

Different compounds require different arrangements.

239 Different chemical compounds require, for the disunion of their elements galvanic arrangements of various powers, and intensities. The decomposition of water is easily effected by a series of fifty pairs of plates, each, one or two inches square. But for some other decompositions, instruments of greater power are required.

Davy's experiments,

Pl. 2.

240. The apparatus employed by Sir H. Davy was extremely simple. Where liquid substances were to be operated upon, he employed occasionally agate and gold cups, *p, n*, fig. 56, each of which was capable of holding about 60 grains of water. These were connected by fibres of amianthus, *a* and into each was inserted a platinum wire. The wires were connected with the two extremities of a powerful galvanic series.

On solids,

Pl. 2.

241. Solid bodies were submitted to the galvanic influence, either by immersing small pieces of them in gold cones, *p, n*, fig. 57 ; or, at other times, by making cups of the substance intended to be decomposed. Or if it was desirable to preserve them from contact with water, they were laid on a small insulated dish of platinum, with the inferior surface of which, immediately under the substance used, a wire from one end of the battery was connected, while the substance itself was made to communicate by another wire, with the opposite extremity of the apparatus.

On solutions.

242. When the gold cones were both filled with a solution of sulphate of potassa (a salt composed of potassa and sulphuric acid,) after exposure, during a sufficient time, to a powerful galvanic arrangement, pure potassa was found in the negative cup, and sulphuric acid in the positive. The decomposition was quite complete, no acid being found in one cone, and no alkali in the other.

The experiment was repeated with several other neutral salts, and with the invariable result, that the acid collected in the positive cone, and the alkali in the negative one.

Decomposition of insoluble bodies.

243. Salts which are either insoluble, or very sparingly soluble in water, had their elements disunited in the following manner. Cups were constructed of them, which were filled with water, and connected by platinum wires with the opposite ends of a galvanic battery, the vessels themselves communicating as before, by means of moistened amianthus. At the conclusion of the experiment sulphuric acid (when the cups were made of sulphate of lime) was found in the positive cup, and lime water in the negative one. Sulphate of strontia, fluuate of lime, and sulphate of baryta, were decomposed, though less easily, by the same expedient. In all these cases the acid element was found at the positive side, and the earthy one at the negative side, of the arrangement.

244. These facts evidently point out a transference of the elements of combination from one electrified vessel, or surface, to another differently electrified. The principle may be made much more apparent by a little variation of the experiment.

Transfer of the elements,

Thus, if solution of sulphate of potassa be electrified in the positive cup *p*, fig. 56, water alone being contained in *n*, after a sufficient continuance of the electrical action, *p* will be found to contain diluted sulphuric acid, and the potassa will be discovered in the water of *n*. The alkali must necessarily, therefore, have passed, in an imperceptible form, along the connecting amianthus *a*, from the vessel *p* to the vessel *n*. Reversing the experiment, and filling *n* with solution of sulphate of potassa, the alkali remains in this cup; and the acid is transferred to the opposite side *p*. In one experiment, in which nitrate of silver was placed in the positive cup, and pure water in the negative one, the whole of the connecting amianthus was covered with revived silver.

Pl. 2.

Acid to positive, alkali to negative,

245. In the farther prosecution of the inquiry, Sir H. Davy succeeded in discovering a still more extraordinary series of facts. When an intermediate vessel (*i*, fig. 47) was placed between the positive and negative cups *p* and *n*, and was connected with both of them by moistened amianthus, it was found, that acids may actually be made to pass from *n* to *p*, through the intermediate solution in *i*, without combining with it. Thus solution of sulphate of potassa being put into the negative cup *n*, solution of pure ammonia into *i*, and pure water into *p*; in half an hour, sulphuric acid was found in the water of the positive cup, to have reached which it must have been transferred from *n* through the intermediate solution of ammonia. Muriatic acid, also, from muriate of soda, and nitric acid from nitrate of potassa, were transferred from the negative to the positive side through an interposed solution of alkali. And contrariwise, alkalies and metallic oxides were transmitted from the positive to the negative side, through intervening solutions of acids.

Pl. 2.

pass through an intermediate solution,

Exp.

It is necessary, however, that the solution, contained in the intermediate vessel *i*, should not be capable of forming an insoluble compound with the substance intended to be transmitted through it. Thus sulphuric acid, in its passage, from sulphate of potassa in the negative cup, through the vessel *i* containing a solution of pure baryta, is detained by the baryta, and falls down in the state of an insoluble compound with that earth.

Circumstances to be attended to.

246. Bodies, the composition of which is considerably more complicated, are, also, decomposed by voltaic electricity. Thus, from certain minerals, containing acid and alkaline matter in only very minute proportion, these ingredients are separately developed. Basalt, for example, (a kind of stone, which, in 100 grains, contains only $3\frac{1}{2}$ grains of soda and half a grain of muriatic acid,) gave, at the end of ten hours, evident traces of alkali round the negative, and of acid round the positive wire. A slip of glass, also, negatively electrified in one of

Decomposition of minerals,

Of glass.

the gold cones, had soda detached from it, and sustained a loss of weight.

Alkali and acid derived from the impurities of water.

247. It may now be understood, why, by the agency of galvanism on water, alkali appears at the negative and acid at the positive wire. The fact was, for some time, not a little perplexing to Sir H. Davy; till, at length, he ascertained, that all water, however carefully distilled, contains neutral salts in a state of solution. From these impurities, the alkaline and acid elements are separated, agreeably to a law which has already been explained. In the same way, also, the muriatic acid and alkali are accounted for, which some chemists have obtained by galvanizing what was before considered as pure water; a fact which has been urged in proof of the synthetical production of both those bodies. Absolutely pure water, it has been demonstrated by Sir H. Davy, yields nothing but hydrogen and oxygen gases.

Similar effects of ordinary electricity.

Pl. 2.

248. All the effects of galvanic arrangements, in producing chemical decompositions, it has been found, may be obtained by ordinary electricity. Its adaption to this purpose was first successfully attempted by Dr Wollaston.* The apparatus, which he employed, was similar to that already represented, fig. 46. *a*, excepting that the wires instead of being exposed to the fluid, contained in the tube, throughout their whole length, were covered with wax, and the points only were laid bare. Or (what was found to answer still better) the wires were enclosed in capillary tubes, which were sealed at their extremities, and then ground away, till the points alone were exposed. The conducting wires, thus arranged, were then introduced into a tube, or other vessel containing the liquid to be operated on, and were connected, the one with the positive, the other with the negative, conductor of an electrical machine, disposed for positive and negative electricity† When solution of sulphate of copper was thus electrized, the metal was revived round the negative pole. On reversing the apparatus, the copper was re-dissolved, and appeared again at the other wire, now rendered negative.

When gold wires, from $\frac{1}{700}$ to $\frac{1}{1500}$ of an inch in diameter, thus enclosed, were made to transmit electricity, a succession of sparks afforded a current of gas from water. When a solution of gold in nitro-muriatic acid was passed through the capillary tube; the tube then heated to drive off the acid; and afterwards melted and drawn out, it was found that the mere current of electricity, without sparks, evolved gas from water.

Sir H. Davy has since proved, that, by a similar apparatus, solution of sulphate of potassa is decomposed, potassa appearing at the negative, and sulphuric acid, at the positive pole.‡ H. 1. 187.

* *Philos. Trans.* 1801.

† See Cuthbertson's *Practical Electricity*.

‡ *Philos. Trans.* 1806.

249. All bodies which exert powerful chemical agencies upon each other when freedom of motion is given to their particles, render each other oppositely electrical when acting as masses. Hence Sir H. Davy, the great and successful investigator of this branch of chemical philosophy, has supposed that electrical and chemical phenomena, though in themselves quite distinct, may be dependent upon one and the same power, acting in the former case upon masses of matter, in the other upon its particles.

Davy's idea of the connection between chemical attraction and galvanism.

250. The power of the Voltaic apparatus to communicate divergence to the electrometer, is most observed when it is well insulated and filled with pure water; but its power of producing ignition and of giving shocks, and of producing the other effects observed when its poles are connected, are much augmented by the interposition of dilute acids, which act chemically upon one of the plates: here, the insulation is interfered with by the production of vapour, but the quantity of electricity is much increased, a circumstance which may, perhaps, be referred to the increase of the positive energy of the most oxidable metal by the contact of the acid. In experiments made with the great battery of the Royal Institution, it has been found that 120 plates rendered active by a mixture of one part of nitric acid and three of water, produced effects equal to 480 plates rendered active by one part of nitric acid and fifteen of water.

Circumstances promoting the power of the Voltaic apparatus.

251. In the Voltaic pile, the *intensity* of the electricity increases with the number of alternations, but the *quantity* is increased by extending the surface of the plates.* Thus, if a battery, composed of thirty pairs of plates two inches square, be compared with another battery of thirty pairs of twelve inches square, charged in the same way, no difference will be perceived in their effects upon bad or imperfect conductors; their powers of decomposing water and of giving shocks will be similar; but upon good conductors the effects of the large plates will be considerably greater than those of the small: they will ignite and fuse large quantities of platinum wire, and produce a very brilliant spark between the charcoal points. The following experiment will illustrate the different effects of quantity and intensity in the Voltaic apparatus.

Arrangement for intensity and quantity.

Immerse the platinum wires connected with the extremity of a charged battery composed of twelve-inch plates into water, and it will be found that the evolution of gas is nearly the same as that occasioned by a similar number of two inch plates.

Experimental illustration.



* Two or more troughs containing small plates may easily be made to act as one trough of large plates. For this purpose they must be placed with their sides together, their similar ends being in the same direction, and they should be connected by two thick pieces of copper or lead wire, bent

according to the figure, in such a manner that the lower angles of one piece will enter the terminal cells at one end of the battery and the lower angles of the other piece the terminal cells at the other end; the projecting terminations of the wires are to be used as the poles of the battery. *Faraday.*

Apply the moistened fingers to the wires, and the shock will be the same as if there were no connection by the water. While the circuit exists through the human body and the water, let a wire attached to a thin slip of charcoal be made to connect the poles of the battery, and the charcoal will become vividly ignited. The water and the animal substance discharge the electricity of a surface probably not superior to their own surface of contact with the metals; the wires discharge all the residual electricity of the plates; and if a similar experiment be made on plates of an inch square, there will scarcely be any sensation when the hands are made to connect the ends of the battery, a circuit being previously made through water; and no spark, when charcoal is made the medium of connexion, imperfect conductors having been previously applied.

Mr Children's
battery.

These relative effects of quantity and intensity were admirably illustrated by the experiments instituted by Mr Children, who constructed a battery, the plates of which were two feet eight inches wide, and six feet high. They were fastened to a beam suspended by counterpoises from the ceiling of his laboratory, so as to be easily immersed into or withdrawn from the cells of the acid. The effects upon metallic wires and perfect conductors were extremely intense; but upon imperfect conductors, such as the human body, and water, they were feeble.*

252. One of the most convenient methods of constructing a battery of extensive surface has been contrived by Dr Hare, fig. 59, who has given the instrument the name of Calorimotor.

Pl. 2.

Dr Hare's
improvement.

Calorimotor.

A *a*, represent two cubical vessels, twenty inches square, inside. *b b b b*, a frame of wood containing 20 sheets of copper, and 20 sheets of zinc, alternating with each other, and about half an inch apart. *T T t t*, masses of tin cast over the protruding edges of the sheets which are to communicate with each other. Fig. 60, represents the mode in which the junction between the various sheets and tin masses is effected. Between the letters *z z*, the zinc only is in contact with the tin masses. Between *c c* the copper alone touches. It may be observed, that, at the back of the frame, ten sheets of copper between *c c*, and ten sheets of zinc between *z z*, are made to communicate, by a common mass of tin extending the whole length of the frame, between *T T*: but in front, as in fig. 59, there is an interstice between the mass of tin, connecting the ten copper sheets, and that connecting the ten zinc sheets. The screw forceps, appertaining to each of the tin masses, may be seen on either side of the interstice: and likewise a wire for ignition held between them. The application of the rope, pulley, and weights is obvious. The swivel at *S* permits the frame to be swung round and lowered into water in the vessel *a*, to wash off the acid, which, after immersion in the other vessel, might continue to act on the sheets, encrusting them with oxide. Between *p p*, there is a wooden partition, which is not necessary, though it may be beneficial.

When the copper and zinc surfaces are united by an intervening wire, and the instrument is immersed in the acid liquor in the vessel beneath, the wire becomes intensely ignited, and when hydrogen is liberated in sufficient quantity it usually takes fire producing a very beautiful corruscating flame upon the surface of the liquid.†

* *Philos. Trans.* 1815, p. 363.

† See *Amer. Jour. of Science*, vol. 1. 413.

253. When the extremes of a battery composed of large plates are united by wires of different metals, it is found that some are more easily ignited than others, a circumstance which has been referred to their conducting powers: thus, platinum is more easily ignited than silver, and silver, than zinc. If the ignition be supposed to result from resistance to the passage of electricity, we should say that the zinc conducted better than silver, and the silver than platinum.

Metallic
fusion.

254. An important improvement has been suggested in the construction of the Voltaic apparatus by Dr WOLLASTON,* by which great increase of *quantity* is obtained without inconvenient augmentation of the size of the plates: it consists in extending the copper plate, so as to oppose it to every surface of the zinc, as seen in fig. 61. A is the rod of wood to which the plates are screwed; BB the zinc plates connected as usual with the copper plates CC, which are doubled over the zinc plates, and opposed to them upon all sides, contact of the surfaces being prevented by pieces of wood or cork placed at DD.

Wollaston's
improvement.

Pl. 3.

With a single pair of plates of very small dimensions constructed upon this principle, Dr Wollaston succeeded in fusing and igniting a fine platinum wire. By some this is considered the most economical and useful form of the Voltaic apparatus; particularly for all those researches in which there is an occasional demand for quantity as well as intensity of electricity.

Fig. 62, represents the improved form of the Voltaic apparatus of Dr Hare, which he has called a Deflagrator. It consists of four troughs *a a*, *b b*, each 10 feet long. Each two of the troughs are joined lengthwise, edge to edge, so that when the sides of the two *b b* are vertical, those of the others *a a* are horizontal. The troughs are supported by a frame *c c*, and turn upon pivots, *d d*. The pivots are made of iron coated with brass or copper, and a communication is made between these and the galvanic series within by strips of copper, *e*. The galvanic series of 300 pairs of copper and zinc plates (connected as in figs. 63 and 64, each zinc plate *z* being between two copper plates *c c*), are placed in the troughs *a a*.† The acid liquor is contained in the troughs *b b*, and by a partial revolution of the apparatus is made to flow into the troughs containing the plates.‡

Pl. 3.

Dr Hare's
Deflagrator.

255. The theory of the Voltaic pile is involved in many difficulties. The original source of electricity appears to depend upon the contact of the metals, for we know that a plate of silver and a plate of zinc, or of any other difficultly and easily oxidable metals, become negative and positive on contact. The accumulation must be referred to *induction*, which takes place in the electrical column through the very thin stratum of air or paper, and through water when that fluid is interposed between the plates. Accordingly we observe that the apparatus is in the condition of the series of conductors with interposed air and of the Leyden phials, (214.) When the electrical column is insu-

Voltaic pile
operates upon
the principle
of induction.

* *Annals of Philosophy*, Sept. 1815.

† The plates are not represented in the lower trough, in order that the interior may be better understood.

‡ See *American Jour. of Science*, vol. 3, p. 347.

§ Another form is described by Prof. De Butts, *Ibid.* vol. viii. p. 271—and one by M. Hart in *Brewster's Jour.* vol. 4.

lated the extremities exhibit feeble negative and positive powers, but if either extremity be connected with the ground, the electricity of its poles or extremities is greatly increased, as may be shown by the increased divergence of the leaves of the electrometer which then ensues.

Electricity continually active in nature.

256. As general changes in the form and constitution of matter are connected with its electrical states, it is obvious that electricity must be continually active in nature. Its effects are exhibited on a magnificent scale in the thunder-storm, which results from the accumulation of electricity in the clouds, as was first experimentally demonstrated by Dr Franklin, who also first showed the advantage of pointed conductors as safeguards for buildings.

Arrangements of organic substances admit of producing electrical effects.

257. That arrangements of different organic substances are capable of producing electrical effects, has been shown by various experimentalists. If the hind legs of a frog be placed upon a glass plate, and the crural nerve dissected out of one, made to communicate with the other, it will be found, upon making occasional contacts with the remaining crural nerve, that the limbs of the animal will be agitated at each contact. These circumstances have induced some physiologists to suppose that electricity may be concerned in some of the most recondite phenomena of vitality, and Dr Wollaston, Sir E Home, and Prof. Brande, have made some experiments tending to confer probability on this idea.*

Electricity concerned in the phenomena of vitality.

258. We have as yet no plausible hypothesis concerning the *cause* of electrical phenomena, though the subject has engaged the attention of the most eminent philosophers of Europe. They have been by some referred to the presence of a peculiar fluid existing in all matter, and exhibiting itself by the appearances which have been described, whenever its equilibrium is disturbed, presenting negative and positive electricity when deficient and when redundant. Others have plausibly argued for the presence of two fluids, distinct from each other. Others have considered the effects as referable to peculiar exertions of the attractive powers of matter, and have regarded the existence of any distinct fluid or form of matter to be as unnecessary to the explanation of the phenomena, as it is in the question concerning the cause of gravitation.

Theories.

Experiments seeming to favour one more than another.

259. When the flame of a candle is placed between a positive and negative surface, it is urged towards the latter; a circumstance which has been explained upon the supposition of a current of electrical matter passing from the positive to the negative pole; indeed, it has been considered as demonstrating the existence of such a current of matter. But if the flame of phosphorus be substituted for that of a candle, it takes an opposite direction; and, instead of being attracted towards the negative, it bends to the positive surface. It has been shown that inflammable bodies are always attracted by negative surfaces, and acid

* *Philos. Trans.* 1809.

bodies, and those in which the supporters of combustion prevail, are attracted by positive surfaces. (236.) Hence the flame of the candle throwing off carbon, is directed to the negative pole, while that of phosphorus forming acid matter goes to the positive, consistently with the ordinary laws of electro-chemical attraction.*

260. There are other experiments opposed to the idea that electricity is a material substance. If we discharge a Leyden phial through a quire of paper, the perforation is equally burred upon both sides, and not upon the negative side only, as would have been the case if any material body had gone through in that direction. The power seems to have come from the centre of the paper, as if one half of the quire had been attracted by the positive, and the other by the negative surface.

Experiments in opposition to electricity being material.

261. When a pointed metallic wire is presented towards the conductor of the electrical machine, in a darkened room, a star of light is observed when the conductor is positive, but a brush of light when it is negative; a circumstance which has been referred to the reception of the electric fluid in the one case, and its escape in the other. In the Voltaic discharge the same appearances are evident upon the charcoal point, rays appearing to diverge from the negative conductor, while upon the positive a spot of bright light is perceptible. But these affections of light can scarcely be considered as indicating the emission or reception of any specific form of matter.

One of a contrary tendency.

262. It has been long known that the copper sheathing of vessels corrodes rapidly in sea water, being converted into an oxide through the medium of some acid, or at least of a decomposed substance, occupying the negative extremity of the electric scale. The copper must therefore be positive in respect to the body decomposed or attracted. Sir H. Davy inferred that if a substance more positive than copper, and in contact with it, could be exposed to the corroding action, that the copper would, by induction, be rendered less positive, and therefore indisposed to combine with any other negative body.† This he effected by bringing copper in contact with zinc or iron. A piece of zinc as large as a pea, or the head of a small round nail, was found adequate to preserve 40 or 50 square inches of copper. It is necessary, however, that the copper be not rendered too strongly negative, otherwise the positive electric bodies, such as magnesia and lime, separate from the water, adhere to the copper and form a nidus for sea weeds and shell-fish. This happens when there is 1-35th to 1-80th of the protecting metal. With 1-150th no such deposits were noticed.

Application of galvanism to preserve copper sheathing.

On the same principle he has proposed the use of protectors for steam boilers where salt water is used.‡ And Mr Pepys has suggested the preservation of iron or steel instruments from rust by contact with a piece of zinc.

* *Phil. Trans.* 1824, &c.

† *Philos. Mag.* N. S. iii. 59.

‡ *Phil. Trans.* 1826, Part iii.

CHAPTER II.

OF ELECTRO-NEGATIVE SUBSTANCES.*

Electro-nega-
tive, or
acidifying
principles.

263. The substances belonging to this class are characterized by possessing very energetic powers of combination in respect to the simple inflammable bodies, and they are each of them capable of producing acids, whence they may also be termed *acidifying* principles. When their compounds are submitted to electro-chemical decomposition, these elements are attracted by the positive surface ; hence their natural or inherent electrical states may be considered as negative.

These acidifying, electro-negative substances are five in number :

1. Oxygen.
2. Chlorine.
3. Bromine.
4. Iodine.
5. Fluorine.

SECTION I. *Nomenclature.*

Chemical
nomencla-
ture.

264. These bodies enter into combination with each other, and with other bodies, to be hereafter described, producing compounds, in an account of which it will be necessary to make use of the peculiar language of chemistry. The following examples may serve to give some idea of the principles of nomenclature generally adopted in chemistry.

Oxygenation.

When any body unites with oxygen, whatever the product may be, the process is termed *oxygenation*. When only a certain portion of oxygen combines with other bodies, the product *not* acquiring *acid* properties, the process is termed *oxidation*, and the new compounds are usually distinguished by the termination *ide*,—as oxide of chlorine, *oxide* of nitrogen. In like manner similar combinations of chlorine, bromine, and iodine, are distinguished as *chlorides*, *bromides* and *iodides*—thus we have *chloride* of sulphur, *iodide* of iron, &c.

Oxidation.

Compounds
with smallest
proportions of
oxygen,

When more than one compound of this kind is produced, the terminations *ous* and *ic* are used to designate the relative proportions of the electro-negative substances. Thus nitrogen forms two oxides ; that containing the smallest proportion of oxygen is the *nitrous* oxide, that containing the largest the

* By some termed *simple supporters of combustion*.

nitric oxide. The acid compounds are similarly designated, as *nitrous* and *nitric acid* ; *sulphurous* and *sulphuric acid* ; and where there are intermediate compounds the term *hypo* is occasionally added to the acid next above it in point of oxidization. Thus, *hyposulphuric acid* signifies an acid compound intermediate between sulphurous and sulphuric acids ; *hypophosphorous acid*, an acid containing less oxygen than the phosphorous acid.

Acid compounds,

The different combinations of the metals with oxygen, are perhaps best distinguished by prefixing to the word *oxide* the first syllable of the Greek ordinal numerals, as originally proposed by Dr Thomson. Thus the *protoxide* of a metal will denote the compound containing a minimum of oxygen, or the first oxide which the metal is capable of forming ; *deutoxide* will denote the second oxide of a metal, &c. ; and when a metal is combined with the largest possible quantity of oxygen, the compound, if not acid, is called *peroxide*. The same rule applies to the *chlorides* and *iodides*.

Metals and oxygen, &c.

The acids terminating in *ous* produce compounds in which the termination *ite* is used ; while those ending in *ic* form compounds in which the ending *ate* is used. Thus the combination of sulphurous acid and potassa, is a *sulphite* of potassa ; that of sulphuric acid and potassa, a *sulphate* of potassa, &c.

When the same acid combines with more than one oxide of the same metal, the first syllable of the Greek ordinal numeral is in that case applied to the acid ; thus, the *protosulphate* and *persulphate* of iron signify the combinations of sulphuric acid with the protoxide and peroxide of iron. The term *oxysulphate* is occasionally used to designate the latter compound, and in the same sense we speak of *oxynitrates*, *oxyphosphates*, &c. but the former mode of designation is less equivocal.

Same acid with several oxides.

The compounds of the simple inflammable bodies with each other, and with the metals, are commonly designated by the termination *uret*, as *sulphuretted* of phosphorus, *phosphuretted* of carbon, *carburetted* of iron, *bromuretted* of silver, &c.

Simple inflammables.

The terms *bi sulphuretted*, *bi sulphate*, *bi phosphuretted*, *bi phosphated*, &c. applied to compounds, imply that they contain twice the quantity of sulphur, sulphuric acid, phosphorus or phosphoric acid, existing in the respective sulphuretted, sulphate, phosphuretted and phosphate.

265. The term *Gas* is applied to all permanently elastic fluids, except the atmosphere, to which the term air is appropriated.

Gases.

For performing the necessary experiments on gases, many articles of apparatus are necessary, consisting partly of vessels fitted for containing the materials that afford them, and partly of vessels adapted to the reception of gases, and for submitting them to experiment.

Apparatus for gases ;

For procuring such gases as are producible without a very strong heat, glass bottles, furnished with ground stoppers and bent tubes, are sufficient, fig. 65. Of these, several will be re-

for procuring gases ;
Pl. 3.

quired of different sizes and shapes, adapted to different purposes. If these cannot be procured, a Florence flask, with a cork perforated by a bent glass tube, or even by a tin pipe, will serve for obtaining some of the gases.

Those gases, that require, for their liberation, a red heat, may be procured by exposing to heat the substance capable of affording them, in coated earthen retorts or tubes; or in a gun barrel, the touch-hole of which has been accurately closed by an iron pin. To the mouth of the barrel must be affixed a glass tube, bent so as to convey the gases where it may be requisite.

Pl. 3.

A very convenient apparatus, for obtaining such gases as cannot be disengaged without a red heat, consists of a cast-iron retort, having a jointed metallic conducting tube fitted to it by grinding; by means of which the gas may be conveyed in any direction, and to any moderate distance. It is represented as placed, when in actual use, within the bars of a common fire-grate, fig. 66, *a*, *b*.*

for receiving
gases.

For receiving the gases, glass jars, of various sizes, figs. 58, 67 *a* and 78, are required, some of which should be furnished with necks at the top, fitted with ground stoppers. Others should be provided with brass caps, and screws, for the reception of air-cocks, fig. 69. Of these last, (the air-cocks) fig. 70, several will be found necessary; and, to some of them, bladders,† fig. 71, or elastic bottles, should be firmly tied, for the purpose of transferring gases. These jars will also be found extremely useful in experiments on the properties and effects of the gases. Some of them should be graduated into cubical inches, figs. 69 *a* and 72.

Pneumatic
trough.

To contain these jars, when in use, a vessel will be necessary, capable of holding a few gallons of water. This is best made of copper, fig. 67, *b*, if of considerable size; or, if small, of tin, japanned or painted. Fig. 67, *ff* exhibits a section of this apparatus, which has been termed the pneumato-chemical trough, or pneumatic cistern. Its size may vary with that of the jars employed; and, about two or three inches from the top, it should have a shelf, on which the jars may be placed, when filled with air, without the risk of being upset. In this shelf should be a few small holes, fig. 71, to which inverted funnels may be soldered.‡

Graduated
tubes, &c.

A glass tube, about 18 inches long, and three quarters of an inch diameter, fig. 72, closed at one end, and divided into cubic inches and tenths of inches, will be required for ascertain-

* The wrought iron bottles in which quicksilver is imported form a convenient apparatus for this purpose, a gun barrel being screwed into the neck of the bottle.

† A bladder may be made to continue tight for a considerable period by pouring a little oil into it at first, and allowing it to become saturated. Bladders are not perfectly tight to gases, and are less so when dry than when moist; consequently gases should not be retained long in them, and never longer than is absolutely necessary. Hydrogen gas passes more rapidly through them than any other gas.

Gas bags are made of oiled silk, or of two layers of woven material, having between them a thick layer of caoutchouc. Those made of oiled silk are seldom tight, and rapidly increase in porosity. F.

‡ Fig. 73, Pl. 3, represents a very convenient form of this apparatus.

ing the purity of air by nitrous gas. It should be accompanied also with a small measure, containing about two cubic inches, and similarly graduated. For employing the solution of nitrous gas in liquid sulphate of iron, glass tubes, about five inches long, and half an inch wide, divided decimally, are also necessary. Besides these, the experimentalist should be furnished with air funnels, fig. 22, for transferring gases from wide to narrow vessels. Pl. I.

266. An apparatus, almost indispensable in experiments on this class of bodies, is a GAZOMETER, which enables the chemist to collect and to preserve large quantities of gas, with the aid of only a few pounds of water. In the form of this apparatus there is considerable variety ; its general construction and use is as follows. It consists of an outer fixed vessel *d* (fig. 74) and an inner moveable one *c*, both of copper or japanned iron. The latter slides easily up and down within the other, and is suspended by cords passing over pulleys, to which are attached the counterpoise, *ee*. To avoid the incumbrance of a great weight of water, the outer vessel *d* is made double, or is composed of two cylinders, the inner one of which is closed at the top and at the bottom. The space of only about half an inch is left between the two cylinders, as shown by the dotted lines. In this space, the vessel *c* may move freely up and down. The interval is filled with water as high as the top of the inner cylinder. The cup, or rim, at the top of the outer vessel, is to prevent the water from overflowing, when the vessel *c* is forcibly pressed down, in which situation it is placed, whenever gas is about to be collected. The gas enters from the vessel in which it is produced, by the communicating pipe *b*, and passes along the perpendicular pipe, marked by dotted lines in the centre, into the cavity of the vessel *c*, which continues rising till it is full. Gazometer.

To transfer the gas or to apply it to any purpose, the cock *b* is to be shut, and an empty bladder, or bottle of elastic gum, furnished with a stop cock, to be screwed on, *a*. When the vessel *c* is pressed down with the hand, the gas passes down the central pipe, which it had before ascended, and its escape at *b* being prevented, it finds its way up a pipe which is fixed to the outer surface of the vessel, and which is terminated by the cock *a*. By means of an ivory mouth-piece screwed upon this cock, the gas, included in the instrument, may be respired ; the nostrils being closed by the fingers. When it is required to transfer the gas into glass jars standing inverted in water, a crooked tube may be employed, one end of which is screwed upon the cock *b* ; while the other aperture is brought under the inverted funnel, fixed into the shelf of the pneumatic trough. (See fig. 67.) Transferring
of Gases.

Several alterations have been made in the form of this apparatus ; but they are principally such as add merely to its neatness and beauty, and not to its utility ; and they render it less easy of explanation. The counterpoises *ee* are now, generally,

concealed in the framing, and the vessel *c* is frequently made of glass.

Gas-holder.

267. When large quantities of gas are required, (as at a public lecture), the gas-holder, (fig. 75) will be found extremely useful. It is made of copper or tinned iron-plate, japanned both within and without. Two short pipes, *a* and *c*, terminated by cocks, proceed from its sides, and another, *b*, passes through the middle of the top or cover, to which it is soldered, and reaches within half an inch of the bottom. It will be found convenient also to have an air cock with a very wide bore, fixed to the funnel at *b*. When gas is to be transferred into this vessel from the gazometer, the vessel is first completely filled with water through the funnel, the cock *a* being left open, and *c* shut. By means of a horizontal pipe, the aperture *a* is connected with *a* of the gazometer. The cock *b* being shut, *a* and *c* are open, and the vessel *c* of the gazometer (fig 74,) gently pressed downwards with the hand. The gas then descends from the gazometer till the air-holder is full, which may be known by the water ceasing to escape through the cock *c*. All the cocks are then to be shut, and the vessels disunited. To apply this gas to any purpose, an empty bladder may be screwed on *a*; and water being poured through the funnel *b*, a corresponding quantity of gas is forced into the bladder. By lengthening the pipe *b*, the pressure of a column of water may be added: and the gas, being forced through *a* with considerable velocity, may be applied to the purpose of a blow-pipe, &c. &c. The apparatus admits of a variety of modifications. The most useful one appears to be that contrived by Mr Pepys, consisting chiefly in the addition of a shallow cistern (fig. 66, *c*) to the top of the air-holder, and of a glass register tube *f*, which shows the height of the water, and consequently the quantity of gas, in the vessel. When a jar is intended to be filled with gas from the reservoir, it is placed, filled with water, and inverted in the cistern *c*. The cocks 1 and 2 being opened, the water descends through the pipe attached to the latter, and the gas rises through the pipe *e*. By raising the cistern *a* to a greater elevation, any degree of pressure may be obtained; and a blow-pipe may be screwed on the cock at the left side of the vessel.*

Pl. 2.

The gazometer, already described, is fitted only for the reception of gases that are confinable by water; because quicksilver

Precautions.

* It is necessary to be aware of the possible entrance of common air with the water, even when there is considerable depth in the cistern. When the gas is passing rapidly out at the lateral stop-cock, and consequently the water rapidly descending through the tube, it will, if unattended to, frequently acquire a rotary motion, which, from mechanical causes easily explained, will at last produce an aperture commencing at the surface of the water and descending to the very bottom of the tube. Down this, air is rapidly carried by the descending water, which, mixing with the gas in the instrument, deteriorates it, and with inflammable gases may lead to dangerous results. Hence this rotary motion when observed, should be disturbed. The formation of the central channel for air may easily be prevented by allowing a large bung or a piece of light wood to swim on the surface of the water. If rotation does take place, it will draw the floating mass to the centre, and prevent the air from passing down by hindering the formation of a channel, if water be plentifully supplied. F. 352.

would act on the tinning and solder of the vessel, and would not only be spoiled itself, but would destroy the apparatus. Yet an instrument of this kind, in which mercury can be employed, is peculiarly desirable, on account of the great weight of that fluid; and two varieties of the mercurial gazometer have therefore been invented. In that invented by Mr Pepys, the cistern for the mercury is of cast-iron. Mr Newman has joined a gazometer of this kind to an improved mercurial trough, by means of which the advantages of both are obtained with only 60 or 70 pounds of quicksilver,* (fig. 76.)

Mercurial gazometers.

Pl. 3.

268. For those gases that are absorbed by water, a mercurial trough is necessary. For the mere exhibition of a few experiments on these condensible gases, a small trough, eleven inches long, two wide, and two deep, cut out of a solid block of mahogany, (or soapstone) is sufficient.

269. A useful apparatus, *for submitting gases to the action of electricity*, is shown in fig. 77; where *a* represents the knob of the prime conductor of an electrical machine; *b*, a Leyden jar, the ball of which is in contact with it, as when in the act of charging; and *c*, the tube standing inverted in mercury, and partly filled with gas. The mercury is contained in a strong wooden box *d*, to which is screwed the upright iron pillar *e*, with a sliding collar for securing the tube *c* in a perpendicular position. When the jar *b* is charged to a certain intensity, it discharges itself between the knob *a* and the small ball *i*, which, with the wire connected with it, may be occasionally fitted on the top of the tube *c*. The strength of the shocks is regulated by the distance between *a* and *i*.

Pl. 3.

Apparatus for submitting gases to electricity.

By the same apparatus, or the tube, fig. 88, inflammable mixtures of gases may be exploded by electricity.

Pl. 4.

* It is not more than 18 inches in length and height; and it is placed in a large japanned tray to collect scattered mercury.

When gas is to be collected in the gazometer, the beak of the retort is placed below the surface of the mercury, in the cup at the bottom of the apparatus, and having a bell-shaped vessel immersed in the mercury immediately over it. The trough has a cavity in the middle, large enough to fill a jar 10 inches long, and 2.1-2 wide; and there is a shelf on each side, three inches in width, to support vessels containing gas. Opposite to three indentations on the edge of the trough, are three holes in one of the shelves, into which the beaks of retorts liberating gas are to be introduced; or a sliding shelf with apertures may be fitted across the cavity for the same purpose. The gazometer is at one end, *a*, and sunk below the level of the trough. It is capable of containing 50 cubic inches. A tube, connected with the gazometer at the lower part is made to ascend, and passing up through the mercury in a corner of the trough, at about an inch above, it bends down again, and terminates beneath its surface. If the gas is contained in the gazometer, it may be transferred to air-jars in the trough, by filling them with mercury, placing them over the end of the bent tube, and giving pressure to the gazometer. The air will pass from it along the tube into the jar. By the bend in the tube, the mercury is prevented from passing into the lower part of the gazometer, while at the same time the gas is allowed a free passage. All inconvenience is prevented by means of a stop-cock, which shuts off the communication between the receiver and the trough, preventing at the same time the escape of air from the gazometer, and of mercury into it. A sliding shelf is fixed beneath the trough to support a spirit-lamp under a retort, or for other purposes. A detonating tube *b* and spring are also attached to the apparatus by a clamp and screws, and may be fixed on any side of the trough. The whole apparatus is of iron, excepting sometimes the pillars which support it, and which may be of brass.

Newman's mercurial trough.

Quantity of
gas to be de-
tonated.

270. The proportion of gas which may be detonated with safety in a glass tube, depends considerably upon the explosive power of the particular mixture under examination, and also upon the quantity detonated at once. A mixture of oxygen with carbonic oxide expands, when inflamed, with much less force than a mixture of oxygen with hydrogen or olefiant gas, and a large quantity will of course expand with more force than a smaller. But besides considering the efficiency of the tube in resisting the expansive force, occasioned by detonation, the experimenter has also so to proportion the quantity of gas, that whilst expanding there shall be abundant space in the tube to retain the products under their greatest volume and agitation, that no loss may occur. No more gas should be introduced into a tube for detonation than will occupy a sixth of its capacity at common temperatures, and, generally, it will be safer and advisable to employ much less. F. 433.

Method's of
transferring
gases.

271. Previously to undertaking experiments on the gases, it may be well for an unpractised experimentalist to accustom himself to the dexterous management of gases, by transferring common air from one vessel to another of different sizes.

Pl. 3.

1. When a glass jar, closed at one end, is filled with water, and held with its mouth downwards, in however small a quantity of water, the fluid is retained in its place by the pressure of the atmosphere on the surface of the exterior water. Fill in this manner, and invert, on the shelf of the pneumatic trough, one of the jars, which is furnished with a stopper (fig. 58). The water will remain in the jar so long as the stopper is closed; but immediately on removing it, the water will descend to the same level within as without; for it is now pressed, equally upwards and downwards, by the atmosphere, and falls therefore in consequence of its own gravity.

Directions for
practice.

2. Place the jar, filled with water and inverted, over one of the funnels of the shelf of the pneumatic trough. Then take another jar, filled (as it will be of course) with atmospherical air. Place the latter with its mouth on the surface of the water; and on pressing it in the same position below the surface, the included air will remain in its situation. Bring the mouth of the jar beneath the funnel in the shelf, and incline it gradually. The air will now rise in bubbles, through the funnel, into the upper jar, and will expel the water from it into the trough.

3. Let one of the jars, provided with a stop-cock at the top, be placed full of air on the shelf of the trough. Screw upon it an empty bladder; open the communication between the jar and the bladder, and press the former into the water, fig. 71. The air will then pass into the bladder, till it is filled; and when the bladder is removed from the jar, and a pipe screwed upon it, the air may be again transferred into a jar inverted in water.

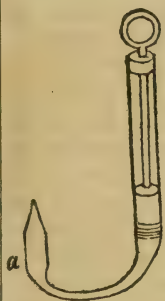
Mr Cavendish's meth-
od.

4. For the purpose of transferring gases from a wide vessel standing over water, into a small tube filled with and inverted in mercury, the following contrivance of Mr Cavendish may

be used. A tube, eight or ten inches long, and of very small diameter, is drawn out to a fine bore, and bent at one end, so as to resemble the Italic letter *l*. The point is then immersed in quicksilver, which is drawn into the tube till it is filled, by the action of the mouth. Placing the finger over the aperture at the straight end, the tube is next conveyed through the water, with the bent end uppermost, into an inverted jar of gas. When the finger is removed, the quicksilver falls from the tube into the trough, or into a cup placed to receive it, and the tube is filled with the gas. The whole of the quicksilver, however, must not be allowed to escape; but a column must be left, three or four inches long, and must be kept in its place by the finger. Remove the tube from the water; let an assistant dry it with blotting paper; and introduce the point of the bent end into the aperture of the tube standing over quicksilver. On withdrawing the finger from that aperture which is now uppermost, the pressure of the column of quicksilver, added to the weight of the atmosphere, will force the gas from the bent tube into the one standing in the mercurial trough.*

272. For the transference of small quantities of gas from one vessel to another, the instrument contrived by Mr Pepys is convenient. It is made of a piece of glass tube, about half an inch in diameter and five inches long, attached to a piece of smaller diameter, which after bending as in the figure, terminates in a chamber at *a*, which being cylindrical for the greater part of its length, terminates in a capillary tube and aperture. A small piston rendered air tight by tow and tallow, is fitted into the cylindrical tube; it is moved by a rod and ring, the rod passing through a box which closes the upper aperture of the instrument, but which should not be air tight. A portion of mercury is placed above the piston, the space between it and the capillary opening of the chamber, is filled with the same metal when the piston is in the position depicted. Upon raising the piston, the mercury follows it, and descends into the chamber *a*, the space left by it being immediately filled with the air or gas which has access to the capillary opening. The rod has a graduation upon it, by which it is known when a tenth of a cubical inch of air has entered the chamber. F. 340.

Mr Pepys' instrument for transference.



is placed above the piston, the space between it and the capillary opening of the chamber, is filled with the same metal when the piston is in the position depicted. Upon raising the piston, the mercury follows it, and descends into the chamber *a*, the space left by it being immediately filled with the air or gas which has access to the capillary opening. The rod has a graduation upon it, by which it is known when a tenth of a cubical inch of air has entered the chamber. F. 340.

273. The manipulation with jars and glasses is comparatively easy to that which occurs in transference from them to tubes, or from tubes to each other. One circumstance with tubes which occasions difficulty, in addition to the narrowness of their

Manipulation with tubes.

* In collecting and transferring gases over quicksilver, especially where the quicksilver is impure or dirty, the gas will escape on the outside of the jar, there being so little adhesion between the quicksilver and the glass, this, I have found, may be guarded against by slightly smearing the edge of the jar with pomatum. W.

mouths, is, their contracted capacity within, by which the easy passage of a bubble of gas upwards, and water downwards, at the same time, is interfered with; this effect is greatest in tubes of the smallest diameters. No great difficulty will occur in the transference of gas from a tube to another that is wider



The second tube is to be filled in the usual manner with water, and held in the well of the trough, in a considerably inclined position; the tube containing the gas is to be brought near it, the upper edge of its mouth inserted as it were into the mouth of the first, and then its position slowly altered, until the gas passing towards the mouth be gradually delivered in distinct bubbles into the first tube. During this transfer, the mouth of the second tube should be retained as much as possible within the first; the latter should not be raised to a perpendicular position, but be considerably inclined, for then the edges of its mouth meet better with, and are adapted to, those of the second tube, so as to confine the gas, and the motion of the bubbles is less sudden and less subject to derangement. Occasionally it is advantageously placed in almost a horizontal position, its closed extremity being but little raised. One bubble of gas should be allowed to rise to some height in the tube before another is permitted to follow.

Transferring
from large to
small tubes,

274. When the delivering tube is larger than the receiving tube, more care is required in the transfer. The first tube should be inclined as before, and the upper edge of the mouth of the second placed within it, and to assist in uniting as it were the two tubes for the moment, the finger and thumb of the left hand (which holds the receiving tube) should be applied at the sides of the junction, so as to confine the gas and prevent its escape laterally. For this purpose, and generally indeed in tube transference, the tube is best held in the hand, with its open extremity passing out between the thumb and fore finger, so that when sustained in the water in an inclined position the back of the hand may be upwards, the hand being as it were over the vessel; the tube is then easily supported by the two or three last fingers of the hand, and the fore finger and thumb are left at liberty to guide the mouths of the vessels, or to close the lateral opening, as has been just described. At other times it may be held as a pen is retained in the hand, the mouth being confined and guided between the thumb and two fore fingers. The tubes should at all times be retained by a light and easy, though secure hold, and not in a stiff rigid manner, and the arms may often be allowed to rest with advantage on the edge of the trough, whilst the hands are immersed in the water.

from jars.

275. An intermediate lipped glass should be used for the transference of gas from a large jar to a tube. The tube being filled with water is to be held under the surface as before described (273); the lip is to be introduced into it, the junction

made by the fingers if necessary, as in the former case, and the gas allowed to pass in distinct bubbles. It will be found easier to transfer from a glass that is from a third to five-sixths full of gas, than from one containing more or less. When a glass is nearly empty, it is often exceedingly difficult to transfer from it into a narrow tube. Advantage may therefore occasionally be taken of the circumstance above mentioned, to replenish the glass with gas.

276. Tubes containing gases are easily transferred from one trough to another, or to other situations, merely by closing their mouths with the finger or thumb, and carrying them to the required situation. The student should very early attain the habit of closing the mouth of a tube by the finger with facility and security. The accurate manipulation of gas in tubes, so that none shall escape and be lost, is often essential in experiments of research, where only small portions of gas are evolved for examination as to many of its properties. F. 326.*

Removing
tubes contain-
ing gas.

277. The method of *weighing gases* is very simple, and easily practised. For this purpose, however, it is necessary to be provided with a good air-pump; and with a globe or flask, furnished with a brass cap and air-cock, as shown fig. 69, *b*. A graduated receiver is also required, to which an air-cock is adapted, as shown at *a*.

Method of
weighing
gases.

Supposing the receiver *a* to be filled with any gas, the weight of which is to be ascertained, we screw the cock of the vessel *b* on the transfer plate of an air-pump, and exhaust it as completely as possible. The weight of the exhausted vessel is then very accurately taken, even to a small fraction of a grain; and it is screwed upon the air-cock of the receiver *a*. On opening both cocks, the last of which should be turned very gradually, the gas ascends from the vessel *a*; and the quantity, which enters into the flask, is known by the graduated scale on *a*. On weighing the vessel a second time, we ascertain how many grains have been admitted. If we have operated on common air, we shall find its weight to be at the rate of about 30,5 grains to 100 cubic inches. The same quantity of oxygen gas will weigh about 34 grains, (33,838 T.) and of carbonic acid gas, upwards of 47 grains, (46,597 T.)

Pl. 3.

278. The specific gravity of any gas compared with common air is readily known, when we have once determined its absolute weight. Thus, if 100 cubic inches of air weigh 30,5 grains, and the same quantity of oxygen gas weighs 33,8888 grains, we say,

Method of de-
termining the
specific grav-
ity of gases.

$$30,5 : 33,8888 :: 1,000 : 1,1111.$$

The specific gravity of oxygen gas will therefore be as 1,1111 to 1,000. We may determine, also, the specific gravity of gases,

* Many operations upon the gases may be performed in apparatus formed partly or altogether of glass tube, for a particular description of which, and for many other details connected with this subject, see the 15th and 16th Sections of Mr Faraday's *Chemical Manipulation*.

more simply, by weighing the flask, first when full of common air, and again when exhausted; and afterwards by admitting into it as much of the gas under examination as it will receive; and weighing it a third time. Now as the loss between the first and second weighing is to the gain of weight on admitting the gas, so is common air to the gas whose specific gravity we are estimating. Supposing for example, that by exhausting the flask it loses 30,5 grains, and that by admitting carbonic acid it gains 46,5972; then

$$30,5 : 46,5972 :: 1,000 : 1,5277:$$

The specific gravity of carbonic acid is therefore 1,5277, air being taken at 1,000. And knowing its specific gravity, we can, without any further experiment, determine the weight of 100 cubic inches of carbonic acid; for as the specific gravity of air is to that of carbonic acid, so is 30,5 to the number required; or

$$1,000 : 1,5277 :: 30,5 : 46,5948.$$

One hundred inches of carbonic acid, therefore, will weigh 46,5948 grains. H. 1. 21.

Circumstances to be attended to.

279. In experiments of this kind, it is necessary either to operate with the barometer at 30 inches, and the thermometer at 60° Fahrenheit, or to reduce the volume of gas employed to that pressure and temperature. Great care is to be taken, not to warm any of the vessels by contact with the hands, from which they should be defended by a glove. On opening the communication between the receiver and the exhausted globe, if any water be lodged in the air-cock attached to the former, it will be forcibly driven into the globe, and the experiment will be frustrated. This may be avoided by using great care in filling the receiver with water, before passing into it the gas under examination. It is also useful to introduce a little piece of crumpled filtering paper into the connecting piece so that when the stop-cock of the globe is screwed on, the paper may lie loosely between the apertures of the two vessels. It will arrest any drops of water that may be carried up.

Correction for pressure.

280. Boyle and Hooke were perhaps the first to observe that the volumes of gases varied inversely in proportion to the pressure exerted upon them, although the law, having been first distinctly announced and enlarged upon by Marriotte, has received his name. Its truth at high pressure although sometimes doubted, has been confirmed by the recent results of Oersted.* Whatever may be the case at high pressure, the law may be considered as accurately true at such pressures as occur naturally and are indicated by the barometer, and also at the greater variations dependent upon the difference of level of the fluid within and without a jar standing over the mercurial or water trough.

Correction for pressure.

281. A pressure of 30 inches of mercury, as observed by an accurate barometer, has been assumed as the *mean height* or

* *Phil. Mag.* lxxviii. 102.

barometric pressure, and volumes of gas observed at any other pressure, frequently require to be corrected to what they would be at this point. For this purpose it is only necessary to compare the *observed height** with the *mean height* or 30 inches, and increase or diminish the observed volume inversely in the same proportion. Thus as the mean height of the barometer is to the observed height, so is the observed volume to the volume required. As an instance, suppose that 100 cubic inches of gas have been observed when the barometer stood at 30,7 inches; then as 30 inches or mean height is to 30,7 inches or observed height, so is 100 or the observed volume to a fourth proportional obtained by multiplying the second and third terms together and dividing by the first: thus $30,7 \times 100 = 3070$, which divided by 30 = 102,333 cubic inches; this would be the volume of the gas at 30 inches of barometric pressure. Or consider the gas as observed at 28,9 inches of the barometer: then 30 inches or mean height is to 28,9 inches or observed height as 100 is to 96,333 cubic inches, that being the result of 28,9 multiplied by 100 and divided by 30, according to the rule.

Examples.

Again, suppose a quantity of gas amounting to 20 cubic inches standing over mercury in a jar, the level of the metal within being 3 inches above that without, and the barometer at 29,4 inches. Then the column of 3 inches of mercury within the jar, counterbalancing 3 inches of the barometric pressure, instead of being 29,4, the latter is effectively only 26,4, and the correction will be as 30 inches is to 26,4 inches, so is the 20 cubic inches observed to 17,6 cubic inches, the volume which the gas would really occupy if the mercury were level within and without the jar, and the barometer were at 30 inches. F. 370.

282. It appears by the experiments of Gay-Lussac and Dalton, that all gases and vapours, of whatever nature, when not in contact with liquids, are affected equally in their volume by changes of temperature, the increase in volume for every additional degree of heat of Fahrenheit's scale, being $\frac{1}{480}$ th part of the volume at 32° F., and the decrease for every diminution of temperature of one degree being also $\frac{1}{480}$ th part of the volume at 32° Fahr. This known, it is easy to calculate how much a volume of gas at a given temperature, 60° Fahr. for instance, would be increased or diminished by a change of one or more degrees. For though it is not for one degree, a $\frac{1}{480}$ th part of the bulk at 60°, the proportion is easily ascertained by adding 28, or the number of degrees of the observed gas above 32° to 480, which producing 508, indicates that $\frac{1}{508}$ th part of the bulk at 60° is to be considered as the increase or diminution for every degree of change. For conceive 480 parts of gas at 32°: at 33° they become 481 parts; at 34°, 482 parts; at 60°, 508 parts; the increase at each degree being $\frac{1}{480}$ th of the volume

Correction temperature.

* If the experiment be continued for some time, the barometer should be observed several times.

at 32° , and consequently such part of the volume at any other temperature, as is indicated by adding the number of degrees above 32° to 480.

Rule.

The rule for correction to be applied to an observed volume of gas, is, therefore, to add to 480 the number of degrees above 32° , to divide the observed volume by this sum, which gives the expansion or contraction for each degree at the observed temperature; to multiply this by the number of degrees between the observed temperature and the temperature to which the gas is to be corrected, which will of course indicate the whole expansion or contraction; and then to subtract this, if the observed be above the corrected temperature, or to add it, if the former be below the latter; thus allowing for the contraction or expansion which would actually take place, if the temperature of the gas were really to be brought to the point to which by calculation it may thus be corrected. For example, suppose 100 cubic inches of gas at 70° Fahr. are to be corrected to mean temperature or 60° . The difference between 70° , the observed temperature, and 32° , is 38, which added to 480 = 518, the 100 inches divided by 518, gives 0,19305 of a cubic inch as the whole expansion for each degree; and this multiplied by 10, the difference between 70° and 60° gives 1,9305 cubic inches as the whole expansion; which subtracted from 100 cubic inches, leaves 98,0690 cubic inches as the volume which would be occupied by the gas at 60° Fahr. F. 376.

283. It is constantly necessary to make corrections both for temperature and pressure in the same volume of gas. It matters not which correction is made first, the result being the same in either mode. Thus for instance, 100 cubic inches observed at the temperature of 40° Fahr. the barometer being at 28 inches, if first corrected for pressure, become 93,33 cubical inches: and then for temperature become 97,158469, which is the true volume. Or, if first corrected for temperature, it becomes 104,09836, and then for pressure, it becomes as before 97,158469 cubic inches. F. 370.*

284. The experiments of Sir H. Davy and Mr Faraday have shown that many substances, which had previously been known, when uncombined, only as gases, may be obtained in a liquid state by generating them under pressure.

Liquefaction
of gases.

When thus compressed, a very moderate heat is sufficient to make them boil; and on the removal of pressure they re-assume the elastic form, most of them with such violence as to cause a report like an explosion, and others with the appearance of brisk ebullition. An intense degree of cold is produced at the same time, in consequence of caloric becoming latent. (158.)

* Dr M. Hall has constructed an instrument, which he calls an Aërometer, intended to give at once a correction for changes in the temperature, in the pressure, in the external and internal heights of the fluid in the pneumatic trough; and when this trough contains water, for the elevation and precipitation of aqueous vapour. See *Quart. Jour.* v. 52.

The process for condensing the gases consists in exposing Process. them to the pressure of their own atmosphere. The materials for producing them are put into a strong glass tube about eight inches long, which is afterwards sealed hermetically ; then, being softened in the flame of a lamp, at about five inches from the closed end, it is to be bent, not sharply, but obtusely and roundly, until the two limbs make an angle of about 130° or 140° . The gas is generated, if necessary, by the application of heat, and when the pressure becomes sufficiently great, the liquid forms and collects in the free end of the tube, which is kept cool to facilitate the condensation.*

285. The pressure required to liquefy the gases is very variable, as will appear from the following table of results obtained by Mr Faraday.

| | Atmospheres. | | | |
|---------------------------|--------------|-----|----|-----------------|
| Sulphurous acid gas | - | 2 | at | 45° F. |
| Sulphuretted hydrogen gas | - | 17 | - | " 50° |
| Carbonic acid | " | 36 | - | " 32° |
| Chlorine | " | 4 | - | " 60° |
| Nitrous oxide | " | 50 | - | " 45° |
| Cyanogen | " | 3,6 | - | " 45° |
| Ammoniacal | " | 6,5 | - | " 50° |
| Muriatic acid | " | 40 | - | " 50° |

Pressure varied.

SECTION II. Of Oxygen.

286. Oxygen has never been obtained in a state of complete Discovery. separation. In the state of gas, it is combined with caloric, and probably with light and electricity. It was discovered in 1774 by Dr Priestley, who gave it the name of *dephlogisticated* air. It was called *Empyreal air*, by Scheele, and *Vital air* by Condorcet.

287. This gas may be obtained from various substances. 1. How obtained.
 From the black or peroxide of manganese, heated to redness in a gun-barrel, or in an iron retort ; or from the same oxide, heated by a lamp in a retort, fig. 67, *c*, or gas bottle, fig. 65, with Pl. 3. half its weight of strong sulphuric acid. One pound of manganese is capable of furnishing from 40 to 50 wine pints of gas. But as manganese is often contaminated with a small proportion of carbonate of lime, it is advisable, before using it, to wash it with muriatic acid diluted with 15 or 20 parts of water ; then with distilled water ; and afterwards to dry it at a moderate heat.

2. From the red oxide of lead (the common red lead) used by painters, heated either with or without half its weight of concentrated sulphuric acid.

* These experiments are dangerous from the bursting of the tubes, and should not be undertaken without attending to the minute directions given by Mr Faraday in Sect. xvi. *Chemical Manipulation.*

3. From various other oxides, as will be hereafter mentioned.

4. From nitrate of potassa (common saltpetre) made red-hot in a gun-barrel, or in a coated earthen retort.

5. From chlorate of potassa heated in a small glass retort, over an Argand's lamp. The oxygen gas thus produced is much purer than that obtained in any other mode, especially the last portions, which should be kept separate. It will be found, also, to be much less contaminated with common air, if heated in a small matrass, which is best when of green glass. The chlorate of potassa may be introduced while the tube is straight, which allows us to make use of one of very small diameter, after this it may be bent by a spirit lamp, as in fig. 49.

Pl. 2.

288. All these substances, after having yielded oxygen gas, are found considerably diminished in weight; and calculating each cubic inch of gas to be equal to one-third of a grain, the loss of weight will be found pretty exactly equivalent to that of gas generated.

Properties of oxygen gas.

289. Oxygen gas is insipid, colourless and inodorous. It is so sparingly absorbed by water, that when agitated in contact with it, no perceptible diminution takes place. It is rather heavier than common air; its specific gravity is 16, hydrogen being assumed = 1.* 100 cubical inches at mean temperature and pressure weigh 33.8888 grains. (T.)

Becomes luminous by compression.

290. It refracts the rays of light less than any other gas. When suddenly and strongly compressed, not only heat is evolved, but the gas *becomes luminous*.

Supports respiration,

291. It is a powerful supporter of respiration and combustion. A small animal, confined in oxygen gas, lives thrice as long as when confined in the same bulk of common air.—This effect seems connected with the absorption of oxygen by the blood.

Exp.

Pass up a little dark coloured blood into a jar partly filled with oxygen gas, and standing over mercury. The gas will be in part absorbed, and the colour of the blood will be changed to a bright and florid red. This change to red may be shown, by putting a little blood into a common vial filled with oxygen gas, and shaking it up. H.

and combustion.

292. All combustible bodies burn in oxygen gas with greatly increased splendour.

Exp.

A lighted wax taper, fixed to an iron wire, and plunged into a vessel of this gas, burns with great brilliancy, fig. 50. If the taper be blown out, and let down into a vessel of the gas while the snuff remains red-hot, it instantly re-kindles, with a slight explosion.

A red-hot bit of charcoal, fastened to a copper wire, and immersed in the gas throws out beautiful sparks.

The light of phosphorus, burnt in this gas, is one of the brightest that can be in any mode produced.

Let the phosphorus be placed in a small hemispherical tin cup, which may be raised by means of the wire stand, fig. 36, two or three inches above the surface

* Its specific gravity according to the latest experiments of Thomson, is 1.1111, that of common air being taken as 1.

of water contained in a broad shallow dish. Fill a bell-shaped receiver, having an open neck at the top, to which a stopper is ground, with oxygen gas; and, as it stands inverted in water, press a circular piece of pasteboard, rather exceeding the jar in diameter, over its mouth. Cover the phosphorus instantly with the jar of oxygen gas, retaining the pasteboard in its place, till the jar is immediately over the cup. When this has been skillfully managed, a very small portion only of the gas will escape. The stopper may now be removed, when the water will rise to the same level within as without the jar, and the phosphorus may be kindled by a heated copper wire.

Combustion of phosphorus.

Pl. 2.

Substitute for the phosphorus a small ball formed of turnings of zinc, in which about a grain of phosphorus is to be enclosed. Set fire to the phosphorus as before. The zinc will be inflamed, and will burn with a beautiful white light. A similar experiment may be made with metallic arsenic, which may be moistened with spirit of turpentine. The filings of various metals may also be inflamed, by placing them in a small cavity, formed in a piece of charcoal, igniting the charcoal, and blowing, on the part containing the metal, a stream of oxygen gas from a bladder, or the gas-holder, fig. 66, d.

Exp.

Of zinc and other metals.

Procure some thin harpsichord wire, and twist it round a slender rod of iron or glass, so as to coil it up in a spiral form. Then withdraw the rod, and tie a little thread or flax round one end of the wire, for about one 20th of an inch; which end is to be dipped into melted sulphur. The other end of the wire is to be fixed into a cork; so that the spiral may hang vertically (fig. 78). Fill, also, with oxygen gas, a bottle capable of holding about a quart, and set it with its mouth upwards. Then light the sulphur and introduce the wire into the bottle of gas, suspending it by the cork. The iron will burn with a most brilliant light, throwing out a number of sparks, which fall to the bottom of the bottle, and generally break it. This accident, however, may frequently be prevented by pouring sand into the bottle, so as to lie about half an inch deep on the bottom. According to Mr Accum,* a thick piece of iron or steel, such as a file, if made sharp pointed, may be burnt in oxygen gas. A small bit of wood is to be stuck upon its extremity, and set on fire, previously to immersion in the gas.

Exp.

A little of Homberg's pyrophorus, a substance to be hereafter described, when poured into a bottle full of this gas, immediately flashes like inflamed gunpowder. H. 1. 208.

Exp.

293. During every combustion in oxygen gas it suffers a considerable diminution.† The fact may be shown, by the combustion of phosphorus, in the manner which has been already described. The first effect of the combustion will be a depression of the water within the jar; but when the combustion has ceased, and the vessel has cooled, a considerable absorption will be found to have ensued.

Oxygen diminished during combustion.

Those persons who are possessed of a mercurial apparatus may repeat this experiment in a less exceptionable manner.

On the surface of the quicksilver, let a small hemispherical cup float, made of tinned sheet-iron; and, in order to keep it from the sides of the jar, it may rest on a wire stand, shaped like the figure 21. Let a jar, the height and diameter of which must be regulated by the size of the mercurial trough, be filled with oxygen gas over water and be removed, by means of a piece of pasteboard, as before described, to the mercurial bath, inverting it dexterously over the tin cup. If the phosphorus had been previously set on fire, a large quantity of the gas, expanded by the heat, would have escaped, and would have prevented the accurate measurement of the absorption. After drying the surface of the mercury within the jar by blotting paper, a portion of the included gas must, therefore, be removed. This is done by an inverted syphon, one leg

Pl. 1.

* Nicholson's *Journal*, 8vo. i. 320.

† To exhibit this, experimentally, in a manner perfectly free from all sources of error, would require such an apparatus as few beside adepts in chemistry are likely to possess. The apparatus required for this purpose is described in the 6th chapter of Lavoisier's *Elements*.

of which is to be introduced (in the same manner as is shown at fig. 79, g) within the jar, before placing it over the mercury; and the gas will be forced through the open extremity of the other, when the jar is pressed down into the quicksilver. When the proper quantity has been expelled, remove the syphon. The cup containing the phosphorus, will thus rest on the surface of the quicksilver within the jar, and above the level of the mercury without. The phosphorus is to be inflamed by passing a crooked iron wire, made red hot, through the quicksilver. On the first impression of the heat, arising from its combustion, the included gas will be considerably expanded; but, when the phosphorus has ceased to burn, a considerable absorption will be found to have taken place, the amount of which may be measured by ascertaining the height of the quicksilver, within the jar, before and after the experiment. The quantity of phosphorus employed should be very small, and should not bear a greater proportion than that of 10 grains to each pint of gas; otherwise the combustion will go on so far as to endanger the breaking of the jar, by the approach of the inflamed phosphorus.

In this process, a white dense vapour is produced, which condenses on the inner surface of the jar in solid flakes. This substance has strongly acid properties; and, being formed by the union of oxygen with phosphorus, is termed the phosphoric acid.

294. The diminution of the volume of oxygen gas, by the combustion of other bodies, may be ascertained in a similar manner. When the substance employed is not easily set on fire, it is proper to enclose, along and in contact with it, a small bit of phosphorus, the combustion of which excites sufficient heat to inflame iron-turnings, charcoal, &c. In the instance of charcoal, however, though that substance undergoes combustion, no absorption ensues; because, as will appear in the sequel, the product is a gas, occupying exactly the same bulk as the oxygen gas submitted to experiment. H. 1. 210.

Stahl's idea
of combustion.

295. The phenomena of combustion were referred by Stahl and his associates, to a peculiar principle which they called *phlogiston*; it was supposed to exist in all combustibles, and combustion was said to depend upon its separation; but this explanation was absurdly at variance with the well-known fact, that bodies during combustion increase in weight.

Bodies increase in
weight.

296. All bodies, by combustion in oxygen gas, acquire an addition to their weight; and the increase is in proportion to the quantity of gas absorbed, viz. about one third of a grain for every cubic inch of gas.—To prove this by experiment, requires a complicated apparatus. But sufficient evidence of this fact may be obtained by the following very simple experiment.

Exp.

Fill the bowl of a tobacco-pipe with iron wire coiled spirally, and of known weight: let the end of the pipe be slipped into a brass tube, which is screwed to a bladder filled with oxygen gas: heat the bowl of the pipe, and its contents, to redness in the fire, and then force through it a stream of oxygen gas from the bladder. The iron wire will burn; will be rapidly oxidized; and will be found, when weighed, to be considerably heavier than before. When completely oxidized in this mode, 100 parts of iron wire gain an addition of about 30.

Theory of
Lavoisier.

297. After the discovery of oxygen gas, it was adopted by Lavoisier as the universal supporter of combustion. The basis of the gas was supposed to unite to the combustible, and the heat and light which it before contained in the gaseous state,

were said to be evolved in the form of flame. But in this case, several requisites are not fulfilled ; the light depends upon the combustible, and not upon the quantity of oxygen consumed ; and there are very numerous instances of combustion in which oxygen, instead of being solidified, becomes gaseous during the operation ; and, lastly, in others, no oxygen whatever is present. Combustion, therefore, cannot be regarded as dependent upon any peculiar principle or form of matter, but must be considered as a general result of intense chemical action. It may be connected with the electrical energies of bodies ; for all bodies which powerfully act upon each other, are in the opposite electrical states of positive and negative ; and the evolution of heat and light may depend upon the annihilation of these opposite states, which happens whenever they combine. B.

Insufficient.

Combustion may be connected with the electrical energies of bodies.

Three classes of products.

298. The substances, capable of uniting with oxygen, afford one or other of the following products ; 1st, an *acid* ; 2dly, an *alkali* or *earth* ; or 3dly, an *oxide*.

299. The name oxygen, from *ὄξος acid* and *γεννάω I generate*, was proposed by Lavoisier, from the supposition that it was the sole cause of acidity. But oxygen is not essential to the acidity of a compound, for some bodies are rendered acid by union with chlorine, others by hydrogen ; and the theory of Lavoisier which considered oxygen as the essential principle of acidity, can no longer be received as correct.* The alkalies and earths are chiefly distinguished, by acting as bases, with which the acids combine, with the loss generally of the separate characters of each (43). The alkalies are soluble in water, and change some vegetable blue colours to green ; and the earths are either not soluble at all or sparingly soluble in that fluid. In some respects the alkalies agree with the 3d class of compounds, viz. oxides.

Oxygen not essential to acidity.

In many instances, a combustible body, which affords an acid when united with a certain quantity of oxygen, gives an *oxide* when combined with a less quantity ; and the acid may be brought back to the state of an oxide by separating part of its oxygen. A few of the metals also, combined with a small proportion of oxygen, give oxides capable of uniting with acids and of composing *salts*, and again united with more oxygen yield an acid which is susceptible, with alkalies and earths, of forming saline compounds. H. 1. 212.

* There can be little doubt, that the heat as well as the light, has its origin partly from the oxygen gas, and partly from the combustible body ; but the precise quantity due to each can scarcely be considered as yet determined.—Lavoisier has endeavoured to prove that a given weight of oxygen abandons very different quantities of heat, when combined with different inflammable bodies. H.

SECTION III. *Of Chlorine.*

Time of discovery.
Synonyms.

300. Chlorine was discovered by Scheele in 1774; it was called by him *dephlogisticated marine acid*. The term *oxymuriatic acid* was afterwards applied to it by the French chemists.

Method of obtaining chlorine.

301. Chlorine gas may be formed by either of the following processes:

1. Into a stoppered retort introduce eight ounces of liquid muriatic acid, sp. gr. 1,160, and four ounces of finely powdered manganese, and apply the heat of a lamp. A gas will be produced which may be received, in the usual manner over water, of the temperature of 80° or 90°. From these materials about 160 cubical inches may be obtained.

Properties of chlorine.

2. Grind together in a mortar eight ounces of muriate of soda (common salt) with three ounces of powdered manganese; put them into a stoppered retort, and pour on them six ounces of sulphuric acid, which have been diluted previously with four ounces of water, and suffered to cool after dilution. On applying a gentle heat, gas will be produced, as in process 1. But as the gas is absorbed by contact with cold water, though not rapidly, it should be received, when it is intended to be kept, in bottles filled with, and inverted in, water of the temperature of 80° or 90° Fahrenheit, and provided with accurately ground stoppers. It will be found also much to diminish the loss of gas by absorption, if it be made to issue from a gas bottle, the tube of which is sufficiently long to reach nearly to the bottom of the inverted receiving bottle, as in fig. 80. The stopper must be introduced under water, while the bottle remains quite full of the gas and inverted, and no water must be left in the bottle, along with the gas.*

Characteristics.

302. Chlorine is an elastic, gaseous fluid, it has a pungent disagreeable odour, and is highly injurious when respired even largely diluted with atmospheric air. When the hand is immersed in the gas a distinct sensation of heat is perceived. Its colour is greenish yellow, hence its name.†

Destroys vegetable colours.

303. Chlorine gas, in its ordinary state, destroys all vegetable colours. This may be shown by passing, into the gas confined by water, a piece of paper stained with litmus, the colour of which will immediately disappear. Hence the application of this gas to the purpose of bleaching, its power of effecting which may be shown by confining, in the gas, a pattern of unbleached calico, which has been previously boiled in a weak solution of caustic potassa, and then washed in water, but not dried. Chlorine gas, however, which has been carefully dried

Exp.

* In some chemical works the proportions of 1 part of manganese, 3 of salt, and 2 of sulphuric acid are recommended, but this mixture is apt to boil over into the neck of the retort.

† From *χλωρος*, green.

by solid chloride of calcium, and into which perfectly dry litmus paper is introduced, produces no change of colour in the litmus, a sufficient proof that its bleaching power depends on the presence and decomposition of water. H. 1. 215.

304. Dry Chlorine, is not condensable by a cold of -40° F.; but either the moist gas, or a solution of chlorine in water, crystallizes at $+40$. The crystals may be obtained by introducing into a clean bottle of the gas, a little water, and exposing the bottle for a few days to a temperature at or below freezing, in a dark place. A solid compound of chlorine and water is formed, which, in a day or two, sublimes and shoots into delicate prismatic needles, extending from half an inch to two inches into the atmosphere of the bottle. When these crystals are put into alcohol, they increase its temperature 8° or 10° , a rapid action takes place, with the formation of much ether and muriatic acid, and a small proportion of a triple compound of chlorine, hydrogen, and carbon. These crystals are composed, according to Mr Faraday, of 36 or 1 atom of chlorine $+90$ or 10 atoms water.

Hydrate of chlorine.

305. Under the pressure of about four atmospheres Mr Faraday discovered that chlorine is a limpid liquid of a bright yellow colour, which does not freeze at the temperature of zero, and which assumes the gaseous form with the appearance of ebullition when the pressure is removed.*

Liquefaction of chlorine.

306. When chlorine is suddenly and considerably condensed by mechanical pressure, not only heat is evolved, as from all other gases, but it emits a weak violet coloured light also. It is not altered by exposure to very high temperatures. By means of the apparatus, fig. 43, Sir H. Davy exposed it to the continued action of charcoal intensely ignited by Voltaic electricity, without the smallest change in its properties.

Pl. 2.

Unaltered in high temperatures.

A glass globe *a*, of about four inches diameter, has at its upper part a sliding wire passing air-tight through a ground collar *b*, to the lower end of which is attached a piece of well burned charcoal *c*: at the bottom is a stop-cock supporting a pair of brass pincers, in which is another pointed piece of charcoal *c*; the globe is exhausted upon the air-pump, filled with chlorine, and the stop-cock *d* and sliding wire *e* attached to the extremities of the Voltaic apparatus; the charcoal points are then brought into contact by pushing down the upper wire, and they are thus retained as long as necessary in intense ignition. B.

Exp.

307. Chlorine is heavier than common air. Its specific gravity is (according to Dr Thomson) 2, 5, (air = 1) which, taking his statement of the sp. gr. of hydrogen, viz. 0,0694 would make it 36 times the weight of hydrogen. 100 cubic inches weigh 76, 25 grains. T.

Specific gravity.

308. At the temperature of 60° , water dissolves or absorbs two volumes of chlorine. The best method of effecting the impregnation of water with this gas is by means of a Woulfe's

Absorbed by water.

* Boston Jour. of Philos. vol. i, p. 516.

apparatus, (fig. 81)* the bottles being surrounded by ice-cold water.

Solution in water.

309. The watery solution if perfectly free from common muriatic acid, has not the usual taste of an acid, but an astringent one. Its purity from muriatic acid may be ascertained by a solution of nitrate of mercury, which is not precipitated by pure chlorine.

Properties.

The watery solution has the colour and peculiar smell of the gas, and has a similar property of discharging vegetable colours. Hence it may be employed in bleaching.

Its use in bleaching.

This may be illustrated by placing a few strips of dyed linen cloth of different colours in a solution of chlorine, the colours will soon be discharged.

Effect of cold,

When the watery solution of chlorine is exposed to a temperature only a little above that of freezing water, the gas, which is combined with it, separates in the form of a liquid, heavier than water.

of heat,

310. Chlorine is not altered by the temperature of boiling water; for its solution may be raised in distillation, and again condensed without change.

of Voltaic electricity.

311. Placed in the current of the electric fluid, the chlorine, and the oxygen of the water, arrange themselves at the positive, and the hydrogen at the negative pole.

A powerful oxidizing agent.

312. Chlorine has a very powerful attraction for hydrogen, and many of the chemical phenomena to which chlorine gives rise, are owing to this property. A striking example is its power of decomposing water by the action of light, or at a red

Woulfe's apparatus.

* In several instances, the substance raised by distillation is partly a condensible liquid, and partly a gas, which is not condensed, till it is brought into contact with water. To effect this double purpose, a series of receivers, termed *Woulfe's apparatus*, is employed. The first receiver (*b*, fig. 81) has a right-angled glass tube, open at both ends, fixed into its tubulure; and the other extremity of the tube is made to terminate beneath the surface of distilled water, contained, as high as the horizontal dotted line, in the three-necked bottle *c*. From another neck of this bottle, a second pipe proceeds, which ends, like the first, under water, contained in a second bottle *d*. To the central neck, a straight tube open at both ends, is fixed, so that its lower end may be a little beneath the surface of the liquid. Of these bottles any number may be employed that is thought necessary.

The materials being introduced into the retort, the arrangement completed, and the joints secured, the distillation is begun. The condensable vapour collects in a liquid form in the balloon *b*, while the evolved gas passes through the bent pipe, beneath the surface of the water in *c*, which continues to absorb it till saturated. When the water of the first bottle can absorb no more, the gas passes, uncondensed, through the second right-angled tube, into the water of the second bottle, which, in its turn, becomes saturated. Any gas that may be produced, which is not absorbable by water, escapes through the bent tube *e*, and may be collected, if necessary.

Supposing the bottles to be destitute of the middle necks, and, consequently, without the perpendicular tubes, the process would be liable to be interrupted by an accident: for if, in consequence of a diminished temperature, an absorption or condensation of gas should take place, in the retort *a*, and, of course, in the balloon *b*, it must necessarily ensue that the water of the bottles *c* and *d* would be forced, by the pressure of the atmosphere, into the balloon, and possibly into the retort; but, with the addition of the central tubes, a sufficient quantity of air rushes through them to supply any accidental vacuum. This inconvenience, however, is still more conveniently obviated by Wether's tube of safety (fig. 82 *b*, *c*), which supersedes the expediency of three-necked bottles. The apparatus being adjusted, as shown by the figure, a small quantity of water is poured into the funnel, so as to about half fill the ball *b*. When any absorption happens, the fluid rises in the ball, till none remains in the tube, when a quantity of air immediately rushes in. On the other hand, no gas can escape, because any pressure from within is instantly followed by the formation of a high column of liquid in the perpendicular part, which resists the egress of gas.—A convenient apparatus for this and similar purposes is described in Brewster's *Edin. Jour.* viii. p. 3.

heat; and most compound substances of which hydrogen is an element, are deprived of that principle, and therefore decomposed in a like manner. For the same reason when chlorine, water, and some other body, which has a strong affinity for oxygen, are presented to one another, the water is resolved into its elements, the hydrogen attaches itself to the chlorine, and the oxygen to the other body. Hence chlorine is indirectly one of the most powerful oxidizing agents.

313. When a burning taper is immersed in a jar of chlorine, the flame becomes red, a dense smoke arises, and the taper is soon extinguished. Phosphorus, and several of the metals, when in a finely divided state, are spontaneously ignited by chlorine and burn in it with much brilliancy.* In these cases binary compounds result, some of which, like those of oxygen, are possessed of acid properties: others are not acid: and such compounds with oxygen being called *oxides*, those which chlorine forms may be termed *chlorides*.

Exp.
Union with combustibles.

314. Chlorine is employed with advantage for the purpose of fumigation, and destroying the volatile principles given off by putrefying animal matter.

315. The presence of chlorine may be detected by a solution of nitrate of silver (lunar caustic) which occasions a dense white precipitate (chloride of silver) which becomes dark on exposure to light, is insoluble in acids and dissolves in pure ammonia.

How detected.

316. Chlorine was once regarded as composed of oxygen and muriatic acid, a fallacy arising from the presence of water, and which will be rendered more intelligible under the head *Muriatic acid*.

Formerly considered as a compound.

317. *Chlorine and Oxygen*.—Chlorine unites with oxygen in four different proportions. The leading character of these compounds is derived from the circumstance that chlorine and oxygen, the attraction of which for most elementary substances is so energetic, have but a feeble affinity for each other. Their union is however regulated by the law of definite proportions; as appears from the following table.

| | Chlorine. | Oxygen. |
|---------------------------------|--------------|---------------|
| Protoxide of Chlorine | 36 or 1 atom | 8 or 1 atom |
| Peroxide of " | 36 " | 32 or 4 atoms |
| Chloric Acid | 36 " | 40 or 5 " |
| Perchloric Acid | 36 " | 56 or 7 " |

318. *Protoxide of Chlorine, or Euchlorine*.—When chlorate of potassa (a salt which will be afterwards described) is distilled, at a gentle heat, with weak muriatic acid, a gas may be collected over mercury, which is found to differ essentially from chlorine. Its colour has a dense tint of brilliant yellow green; and its smell resembles that of burnt sugar, mixed with the peculiar smell of chlorine. Water takes up eight or ten times its volume, and acquires an orange tint. It has been called by its discoverer, Sir H. Davy, *Euchloric gas*, or simply *Euchlorine*. Gay-Lussac has proposed for it the name of oxide of chlorine;

Euchlorine gas.

* The temperature of the gas should not be much below 70° Fahrenheit.

but it may, with more propriety, be called *Protoxide of Chlorine*.

319. Protoxide of chlorine is generally, if not always, best made in a tube retort, formed from a piece of plain glass tube, about half an inch in diameter, two or three inches in length, according to circumstances, and closed at one end. The mouth should be fitted with a good perforated cork, having a small tube fixed into it, which, after proceeding about an inch upwards from the cork, is to turn off nearly at right angles for about three inches, and then return to its first direction for about the eighth of an inch. This piece of tube is the neck of the retort, whilst the wide short piece is the body; the latter having received its charge, the cork is to be put in and made tight by cement, when the distillation may be proceeded with, and the gas evolved and collected.*

Liquefaction.

320. By producing this gas in strong glass tubes hermetically sealed, the unoccupied end of the tube being cooled to 0° F. Mr Faraday obtained it in the form of a very transparent liquid of a deep yellow colour, which was suddenly and violently converted into gas on relieving the pressure.†

Phenomena attending its decomposition.

321. Protoxide of chlorine explodes by a gentle heat, applied to the vessel which contains it. In almost all cases of vivid combustion, there is a condensation of the bodies which unite; but in the decomposition of this gas by heat, we have the remarkable phenomenon of an explosion, accompanied with heat and light, and yet with an expansion of the elements which are separated from each other. H. 1. 217.

Analysis.

It may be analyzed by heating a known quantity of it in a strong tube over mercury. An explosion takes place; and 50 of the gas expand to 60 measures, 20 of which are oxygen, and 40 chlorine. The specific gravity of a gas so constituted must be 2,444, and its composition by weight is, chlorine 36 + oxygen 8. The weight of its atom is consequently 44.

Atomic weight.

When detonated with twice its volume of hydrogen gas, there is a condensation of more than two-thirds of the mixture, and liquid muriatic acid is formed.

* In reference to the distillation of this gas and of all other explosive substances, the student should be aware of the caution required to prevent accidents, in case explosion should occur. Whenever such an effect is probable the vessel should be surrounded with tow or cloth, that if it break the fragments may be retained; and during distillation the side of the apparatus, or that part which is guarded by the tow, is to be turned towards the eyes, that they at least may be out of danger. It is not easy to wrap tow regularly and tightly round a clean glass tube, from its tendency to slip over the surface; but the difficulty is easily obviated, by rubbing the outside of the tube with soft cement, or a very little turpentine with a piece of tow or cloth, so as to render it slightly adhesive to the fingers. Faraday p. 409.

Prof. Silliman prefers placing the materials for producing the gas in a small glass flask furnished with a tube bent twice at right angles, and passing to the bottom of any clean dry phial, flask, or tube, rather deep with a narrow neck, a gentle heat, applied beneath the flask, soon disengages the euchlorine gas, which, by its great weight, displaces the common air from the recipient, and takes its place. By using tongs, properly curved, so as to embrace the phials or tubes filled with the gas, the operator may perform all the necessary experiments, without danger of causing an explosion by the warmth of the hand. *Amer. Jour.* vi. 165.

† *Phil. Trans.* 1823.

322. Mercury has no action on the protoxide of chlorine at common temperatures, antimony and copper burn in it, if introduced previously heated. Sulphur and phosphorus decompose it; and charcoal, already ignited, burns in it with a dull red light. Nitrous gas condenses it with red fumes. It destroys vegetable colours; but first gives the blue a tint of red. Properties.

323. *Per-oxide of Chlorine.*—The per-oxide of chlorine was discovered by Sir H. Davy in 1815,* and soon after by Count Stadion of Vienna,† it is formed by the action of sulphuric acid on the chlorate of potassa. Peroxide of chlorine.

324. To procure it, 50 or 60 grains of the powdered chlorate of potassa, are to be mixed with a small quantity of concentrated sulphuric acid. When thoroughly incorporated, a solid mass will result, of a bright orange colour. This is to be introduced into a very small retort of glass, or a bent tube, which is to be exposed to the heat of water gradually warmed, but prevented from attaining the boiling point, by an admixture of spirit of wine. The gas may be received over mercury, on which it has no action at common temperatures. Method of obtaining it.

325. It has a lively yellow colour, much more brilliant than that of the protoxide; is much more rapidly absorbed by water; and has a peculiar aromatic smell, not mixed with any smell of chlorine. According to Davy, it destroys vegetable blue colours, without first reddening them; but Count Stadion asserts, that it does not change blue paper. When heated to about the temperature of 212° Fahrenheit, or, according to Count Stadion, to between 112° and 114° , it explodes with more violence, and a greater expansion of volume, than the protoxide, producing much light. According to Sir H. Davy, whose result is confirmed by Gay-Lussac, 40 measures of the gas occupy the space of 60 measures after the explosion; of these, 20 are chlorine and 40 oxygen. The per-oxide is therefore composed of 36 or one atom of chlorine united with 32 or 4 atoms oxygen. Its specific gravity must be 2.361. Properties.

326. It is decomposed, at common temperatures, by no combustible body, except phosphorus, which occasions an explosion when introduced into it, and burns, in the liberated gases, with great brilliancy. Composition.

327. Its saturated solution in water, which contains seven volumes of gas, is of a deep yellow colour. It does not taste sour, but extremely astringent and corroding; and it leaves on the tongue a disagreeable and lasting impression. The solution may be kept in the dark unchanged, but, when exposed to the sun's rays, it is decomposed, and chlorine and chloric acid are obtained. H. 1. 218. Decomposed by phosphorus.

328. *Chloric Acid.*—A third compound of chlorine and oxygen was pointed out by Mr Chenevix, some time before it was obtained in a separate form, as existing in the class of salts called hyper-oxyuriates. For the method of exhibiting it in Its solution in water.

* *Phil. Trans.* 1815, Part II.† *Thomson's Annals*, ix. 22.

Method of obtaining it.

a distinct state, we are indebted to Vauquelin* and Gay-Lussac.† The following is the process; To a solution of pure chlorate of baryta, (the mode of preparing which will be hereafter described), add by degrees dilute sulphuric acid, as long as it occasions any precipitation. This separates the baryta, and leaves the chloric acid combined with water only. It is important to add no more sulphuric acid than is barely sufficient; for the slightest excess renders the chloric acid impure. If the right quantity has been used, the liquid obtained should remain perfectly transparent, when, taking two separate portions of it, we add to the one dilute sulphuric acid, and to the other, chlorate of baryta. If either of these agents occasions a precipitate, we must add it by degrees till the effect ceases. The clear liquid is then to be decanted by a syphon, and reserved for use. It is a solution of chloric acid in water; and has the following properties:

Properties.

329. It is colourless, its taste is acid and astringent; and its smell, when concentrated and a little heated, is moderately pungent. It reddens the infusion of litmus. Paper stained with litmus, though it does not immediately lose its colour, yet is deprived of it in a day or two if left in the liquid; or more rapidly if taken out of the liquid and exposed to the air, in consequence of the solution becoming more concentrated. It does not precipitate either silver, mercury, or lead, from their solution in nitric acid. It is volatilized by heat, but not without a partial decomposition into chlorine and oxygen. Hence it afterwards precipitates the nitrate of silver.

Decomposed by muriatic acid, &c.

330. Muriatic acid decomposes it, and both acids, if mixed in just proportion, are changed into chlorine and water.

331. Chloric acid is decomposed, also, by sulphuretted hydrogen and by sulphurous acid. In the first case, chlorine and sulphur are separated, and water is formed. In the second, sulphuric acid is formed, and chlorine set at liberty. None of the acids, which are saturated with oxygen, have any action on chloric acid.

332. All the metals that are capable of decomposing water, decompose also the chloric acid. It combines with the different bases to form the salts called *chlorates*.‡

Composition.

333. According to the experiments of Vauquelin, chloric acid is composed of

| | | | | | | |
|----------|-----------|----|-----------|-----|-----------|-----|
| Chlorine | | 35 | | 100 | | 54 |
| Oxygen | | 65 | | 185 | | 100 |
| <hr/> | | | | | | |
| 100 | | | | | | |

This determination differs materially from that of Gay-Lussac, according to whom 32,304 oxygen convert 28,924 chlorine into chloric acid, and hence it should be composed of

| | | | | | | |
|----------|-----------|------|-----------|-----|-----------|-----|
| Chlorine | | 47.3 | | 100 | | 90 |
| Oxygen | | 52.7 | | 110 | | 100 |
| <hr/> | | | | | | |
| 100. | | | | | | |

* *Ann. de Chim.* xcv. 102.

† *Ibid.* xci. 111.

‡ Formerly called *Hyperoxymuriates*.

The result of Gay-Lussac is by much the more probable of the two, and would make the chloric acid consist of 1 atom of chlorine $36 + 5$ atoms of oxygen $40 = 76$; while Vauquelin's numbers would indicate no less than 8 atoms of oxygen.*

334. *Perchloric Acid*.—The saline matter which remains in the retort after forming the peroxide of chlorine, is a mixture of the perchlorate and bi-sulphate of potassa, and by washing it with cold water, the bisulphate is dissolved and the perchlorate is left. The perchloric acid may be prepared from this salt by mixing it in a retort with half its weight of sulphuric acid, diluted with one third water, and applying heat to the mixture. At the temperature of about 284° F. white vapours rise, which condense as a colourless liquid in the receiver. This is a solution of the perchloric acid. Perchloric acid.

The properties of the perchloric acid have hitherto been little examined. Count Stadion,† its discoverer, found it to be a compound of 1 atom or 36 chlorine + 53 or 7 atoms oxygen, and his analysis has been confirmed by Gay-Lussac.‡ Composition.

SECTION IV. Of Bromine.

In 1826 M. Balard of Montpellier discovered in sea water§ a new substance to which he gave the name *muride*; but it has since been changed to *Bromine*, a word derived from the Greek βρωμος, (*graveolentia*) signifying a strong or rank odour. Discovery.

335. Bromine exists in sea water in the form of hydro-bromic acid. It is present, however, in very small quantity;|| and even the uncrystallizable residue called *bittern*, left after the muriate of soda has been separated from sea water by evaporation, contains but little of it. On adding chlorine to this liquid, an orange yellow tint appears; and on heating the solution to the boiling point, the red vapours of bromine are expelled, which may be condensed by a freezing mixture. A better process is to transmit a current of chlorine gas through the bittern, and then to agitate a portion of ether with the liquid. The ether dissolves the whole of the bromine, from which it receives a beautiful hyacinth red tint, and, on standing, rises to the surface. When the ethereal solution is agitated with caustic potassa, its colour entirely disappears, and on evaporation, cubic crystals Process for obtaining bromine.

* The existence of a simple combination of chlorine and oxygen has been denied by Sir H. Davy, who considers the liquid, obtained by Gay-Lussac, as constituted of two proportions (atoms) of hydrogen, one of chlorine, and six of oxygen. To this, the latter has replied, that the hydrogen is not an element of the acid itself, but of water, with which the acid is united, as is the case with liquid sulphuric and nitric acids. H. 1. 220. See *Ann. de Chim. et de Phys.* Vol. 1.—*Quart. Jour.* 1. 286.

† *Ann. de Chim. et de Phys.* Vol. viii.

‡ *Ibid.* Vol. ix.

§ The original essay of M. Balard was published in the *Annals de Chim. et de Phys.* Aug. 1826, and an abstract of it in the *Edinburgh Jour. of Science*.

|| One hundred pounds of sea water yield but 5 grains of bromide of sodium, or 3,278 grains of bromine. *Quart. Jour.* 1827.

of the hydro-bromate of potassa are deposited. On mixing these crystals, reduced to powder, with pure peroxide of manganese, and adding sulphuric acid diluted with its volume of water, the bromine is disengaged in a gaseous state. A small receiver nearly filled with water is attached to the retort, the beak of which and the receiver are kept cool by a frigorific mixture. The bromine condenses in the beak, runs into the receiver, and falls to the bottom on account of its great specific gravity. It is slightly soluble but the water in its immediate vicinity soon becomes saturated. The water is decanted and the remainder distilled with chloride of calcium, by which the bromine is obtained in a liquid state.

Other sources
of bromine.

M. Balard has also detected bromine in marine plants which grow on the shores of the Mediterranean sea, and has procured it from the ashes of the sea weeds that furnish iodine. He has likewise found it in the ashes of some animals, especially in those of the *Janthina violacea*, one of the testaceous mollusca.

Properties.

336. Bromine at common temperatures is a liquid, the colour of which is blackish red when viewed in mass and by reflected light, but appears hyacinth red when a thin stratum is interposed between the light and the observer. Its odour, which somewhat resembles that of chlorine, is very disagreeable; and its taste powerful. It acts with energy on organic matters, such as wood or cork, and corrodes the animal texture; but if applied to the skin for a short time only, it communicates a yellow stain less intense than that from iodine, and which soon disappears. It is highly destructive to animals, one drop of it placed on the beak of a bird proves fatal.

The specific gravity of bromine is about 3, and its atomic weight 9,411 oxygen being the unit or 75,288 hydrogen being unity.* Its volatility is considerable; for at common temperatures it emits red coloured vapours which are similar in appearance to those of nitrous acid, and at 116,5° F. it boils. It retains its liquid form at 0° F., at 4° below 0° it becomes solid and very hard in an instant.†

Action of
electricity
and heat.

337. Bromine is a nonconductor of electricity, and undergoes no chemical change when transmitted through a red hot glass tube. It is not decomposed by voltaic electricity. It supports combustion in a very feeble manner; a lighted taper immersed in the vapour of bromine is soon extinguished, but before going out it burns a few seconds with a flame which is green at its base and red at its upper part, as in an atmosphere of chlorine.

338. Bromine is soluble in water, in alcohol, and particularly in ether. It does not redden litmus paper, but bleaches it, and it also removes the blue colour from a solution of indigo.

Action on the
metals.

339. The action of bromine on the metals and metallic oxides is similar to that of chlorine; antimony and tin take fire by contact with it, and its union with potassium is attended with

* *Ann. de Chim. Aug. 1826.*

† M. Sécrullas, *Ann. of Philos.* N. S. 1. 395.

a vivid flash of light and explosion. On passing the vapour of bromine over potassa, soda, or lime, a vivid incandescence ensues, oxygen is disengaged, and a metallic bromuret results.

340. When bromine acts on the solution of an alkali or alkaline earth, considerably diluted with water, the bromuret of an oxide is produced, which possesses bleaching properties, and from which acetic acid causes the disengagement of bromine. But when this substance acts upon a concentrated solution of potassa, or when solid potassa is agitated with the ethereal solution of bromine (335), two salts are generated the hydro-bromate and bromate of potassa; and on evaporating the solution the former is obtained in cubic, and the latter in acicular crystals. The bromate of potassa is separated from the hydro-bromate by being very sparingly soluble in cold water.

341. *Bromine and Oxygen*.—Bromine unites with oxygen and forms *Bromic acid*, which may be obtained in a separate state by decomposing a dilute solution of the bromate of baryta with sulphuric acid. From the analysis of the bromate of potassa, it appears to consist of 1 atom of bromine + 5 atoms oxygen.

Bromic acid.

342. The bromates are analogous to the chlorates and iodates. Thus the bromate of potassa is converted by heat into the bromuret of potassium, with disengagement of pure oxygen, deflagrates when thrown on burning coals, and forms with sulphur a mixture which detonates by percussion. The acid of the bromates is decomposed by deoxidizing agents, such as the sulphurous acid and sulphuretted hydrogen. The bromates are decomposed by hydro-bromic and muriatic acids.

Analogous to Chloric and Iodic acids.

343. *Bromine and Chlorine*.—Bromine unites with chlorine at common temperatures, forming a very volatile liquid of a reddish yellow colour, penetrating odour, and exceedingly disagreeable taste. It is soluble in water, without decomposition; the solution bleaches litmus paper without previously reddening it, and has the characteristic odour and colour of the compound. By the action of the alkalies it is resolved into muriatic and bromic acids.

Union with Chlorine.

344. Bromine has a stronger affinity for bases than Iodine, and less strong than Chlorine. From the circumstance of its being intermediate between chlorine and iodine in some of its more important chemical relations, M. Balard at first suspected it to be some unknown compound of these bodies; but as, on further examination, he failed to obtain the least trace of decomposition, he was induced to adopt the opinion that it is an elementary substance. Recent experiments are in favour of this view.*

Affinities.

Undecomposed.

* See those of M. Sérullas, *Ann. de Chim. et Phys.* xxxiv. p. 95.

SECTION V. *Of Iodine.*

Discovery of
Iodine.

345. Iodine was discovered accidentally by M. Courtois, a manufacturer of saltpetre at Paris, in 1812. In the process for procuring soda from the ashes of sea weeds, he found that his metallic vessels were much corroded, and in searching for the cause, he made the discovery of Iodine. Its real nature was soon after determined by Gay-Lussac and Sir H. Davy, each of whom proved that it is a simple non-metallic substance, exceedingly analogous to chlorine.*

Process for
obtaining
Iodine.

346. Iodine is procured by the following process. Lixiviate powdered kelp with cold water. Evaporate the lixivium till a pellicle forms, and set aside to crystallize. Evaporate the mother liquor to dryness, and pour upon the mass half its weight of sulphuric acid. Apply a gentle heat to this mixture in the flask *a* of the *alembic* shown in fig. 83, of which the head or capital *b*, has a tube issuing from it, and descending into the receiver *c*. Fumes of a violet colour arise and condense in the form of opaque crystals, having a metallic lustre, which are to be washed out of the head of the alembic with a small quantity of water, and quickly dried upon bibulous paper.

Pl. 4.

347. Iodine may likewise be obtained from the "*black ash*" of the soap-makers, the residuum of the alkaline matter used in the manufacturing of hard soaps with kelp. Dr Ure has made many experiments with this substance, from which he obtains the Iodine by the following process.

Dr Ure's
process.

The liquid is heated to about 230° F. and poured into a large stone ware basin of which it should fill about one half; sulphuric acid, previously diluted with its own bulk of water, is added till the liquor is saturated. On cooling the mixture a large quantity of saline crystals are found adhering to the sides and bottom of the vessel.† The cold liquid is filtered through a woollen cloth. To every 12 oz. apothecaries' measure 1000 grains of peroxide of manganese, in powder, are added. This mixture is put into a matrass, fig. 84, with a wide neck, over which a glass globe is inverted, and heat is applied with a charcoal chauffer.§ Iodine now sublimes very copiously, and is condensed in the upper vessel. As soon as it becomes warm, another is to be put in its place; and thus the two may be applied in rotation, as long as the violet vapour rises. By this treatment from 80 to 100 grains of iodine may be obtained.

* The original papers on this subject are in the *Annales de Chimie*, vols. lxxxviii. xc. and xci. and in the *Philos. Trans.* for 1814 and 1815.

† When water is poured upon certain bodies for the purpose of extracting their saline ingredients, the process is called *lixivation*, and the solution obtained, a *lixivium*.

‡ These are chiefly composed of soda, a little sulphate of potassa, and a few oblong rhomboidal plates of hydriodate of soda. Sulphur is mixed with these crystals.

§ The less diffusive flame of a lamp is apt to crack the bottom of the matrass, particularly if a large quantity of materials be employed. To prevent the heat from acting on the receiver, a thin disc of wood, having a round hole in its centre, is placed over the shoulder of the matrass.

It is removed from the globes as in the other process. The best subliming temperature is 232° F. U. 513.

348. Iodine is a solid at the ordinary temperature of the atmosphere. It is often in scales resembling those of micaceous iron ore; sometimes in large and brilliant rhomboidal plates; and occasionally in elongated octoëdrons.* Its colour is bluish black; its lustre metallic; it is soft and friable, and a non-conductor of electricity. It produces a yellow stain upon the skin. Its smell resembles that of diluted chlorine. Its taste is acrid. Its specific gravity according to Gay-Lussac is 4,948, but Dr Thomson found it only 3,0844. Properties.

Iodine is fusible at 225° F. and, under the ordinary pressure of the atmosphere, is volatilized at a temperature somewhere near 350° , forming a gas 125 times denser than hydrogen, which last number represents the weight of its atom. According to Gay-Lussac, the specific gravity of its vapour, compared with air, is 8,678. Hence 100 cubic inches should weigh 269 grains.† The volatilization of iodine at the heat of boiling water, which happens when it is distilled with that fluid, depends on its affinity for aqueous vapour. H. 1. 223.

349. The colour of the vapour of iodine is a beautiful violet, and hence its name, (from *ἰώδης*, *violaceus*.)

This may be exhibited by introducing a few scales of iodine into a glass matrass, and heating it over a spirit lamp. Exp.

350. Like chlorine and oxygen, iodine is electro-negative; and therefore attracted by the positive surface of the Voltaic pile. It renders vegetable colours yellow. It is very sparingly soluble in water, that liquid not holding more than $\frac{1}{7000}$ its weight in solution. The colour of the solution is yellow. It is much more soluble in spirit of wine and in ether.

351. Iodine manifests a strong attraction for the pure metals and for most of the simple non-metallic substances. These combinations are termed *Iodides* or *Iodurets*. It is not inflammable; but under favourable circumstances may, like chlorine, be made to unite with oxygen. A solution of the pure alkalies acts upon it in the same manner as upon chlorine, giving rise to the decomposition of water and the formation of the *iodic* and *hydriodic* acids. Combinations with oxygen.

352. *Nature of Iodine.* Iodine, from all that we yet know respecting it, is to be considered as a simple or elementary body. Its discovery lends strong support to that theory, which considers chlorine as a simple body, and muriatic acid as a compound of chlorine and hydrogen. In the property of forming an acid, whether it be united with hydrogen, or with oxygen, iodine bears, also, an analogy to sulphur; and it is remarked by Gay-Lussac of the combinations of chlorine, iodine, and Nature of iodine.

* Dr Wollaston has described the form of its crystal in the *Annals of Philosophy*, V. 237. See also *Quart. Jour.* V. 364.

† The specific gravity of iodine vapour, according to Dr Thomson, is 8,6111, air = 1; 100 cubic inches weigh 262,5308 grains, and its atomic weight, oxygen = 1 is 15,5.

sulphur, with the elements of water, that while the acids, which they respectively form with oxygen, have their elements strongly condensed, those formed with hydrogen have their elements very feebly united. Sulphur has the strongest affinity for oxygen, then iodine, and lastly chlorine. But for hydrogen, chlorine has a stronger attraction than iodine, and iodine than sulphur; whence it appears that the affinity of each of those bodies for oxygen is inversely proportionate to its affinity for hydrogen.

Sources of
iodine.

353. In the state of hydriodic acid, iodine is met with in nature in combination with potassa or soda. Under this form it occurs in many salt and other mineral springs. It has been detected in the water of the Mediterranean sea, in the oyster and some other marine molluscous animals, in sponges, and in most kinds of sea-weed. In some of these productions, such as *Fucus serratus*, and *digitatus*, it exists ready formed, and according to Dr Fyfe,* may be separated by the action of water, but in others it can be detected only after incineration. Vauquelin has found it also in the mineral kingdom, in combination with silver. See *Silver*.

Test for
iodine.

354. The most delicate test of the presence of iodine, is starch, and if added to any liquid containing it, with a few drops of sulphuric acid, a blue compound is formed which is insoluble in water. According to Prof. Stromeyer, a liquid containing but 1-450,000th of its weight of iodine, receives a blue tinge from a solution of starch. Two precautions should be observed to insure success. In the first place the iodine must be in a free state; for it is the iodine itself only, and not its compounds, which unite with starch. Secondly, the solution should be quite cold at the time of adding the starch; for boiling water decomposes the blue compound, and consequently removes its colour.†

Iodic acid.

355. *Iodine and Oxygen—Iodic Acid.*—Iodic acid was discovered about the same time by Gay-Lussac and Sir H. Davy; but the latter first succeeded in obtaining it in a perfectly pure state.‡ When iodine is brought into contact with the protoxide of chlorine, an immediate action ensues, its colour changes to

* *Edin. Philos. Jour.* vol. 1.

† Notwithstanding the delicacy of the test for the presence of iodine afforded by the use of starch, its value is considerably diminished by the facility with which various substances interfere with its action; and this is especially the case when any of those bodies, which either alone or with water, yield hydrogen are present; the iodine becomes hydriodic acid, and the blue colour either disappears, or is not formed. Sulphurous acid and sulphuretted hydrogen, substances almost constantly produced by the incineration of organized bodies, which contain earthy or alkaline sulphates, are especially capable of producing this effect.

Among the various means of obviating this inconvenience is the use of chlorine. M. Balard has been led to apply it in the following manner:—after mixing the liquid containing the iodine with the starch and the sulphuric acid, a small quantity of aqueous solution of chlorine is to be added which from its lightness may be made not to mix with the mixture, but float on the surface; at the place, however, where they touch, a blue zone will be developed where the two solutions are in contact, but if the whole be mixed, it will entirely disappear, if the chlorine be in excess.—*Ann. de Chim.* xxviii.

‡ *Phil. Trans.* 1815.

bright orange, and a liquid is formed.* By the application of a gentle heat, the orange compound of chlorine and iodine is expelled, and a compound of oxygen and iodine remains. This substance is a white semi-transparent solid, volatile at 456° F.; it has no smell, but a strong astringent sour taste. Its specific gravity is such that it sinks in sulphuric acid.

356. When decomposed by heat in a pneumatic apparatus, it is resolved into oxygen gas and pure iodine; and it is therefore termed by Sir H. Davy *oxyiodine*, and by Gay-Lussac *acide iodique anhydre*.†

Decomposition

| | | |
|------------------------------------|----------|----------|
| | Hyd. = 1 | Oxy. = 1 |
| It consists of 5 atoms of oxygen = | 40 | 5 |
| 1 atom of iodine = | 125 | 15,5 |

and the weight of the atom is 165 20,5 T.

357. Anhydrous iodic acid is very soluble in water, and is slightly deliquescent. Its solution, called by Gay-Lussac *acide iodique*, first reddens, and then destroys vegetable blues, and reduces other vegetable colours to a dull yellow. When evaporated sufficiently, it becomes a thick pasty substance, and at length, by a cautiously regulated heat, yields the anhydrous acid unaltered.

Solution of iodic acid.

358. When heated in contact with inflammable bodies, or with the more combustible metals, detonations are produced. Its solution in water rapidly corrodes all the metals, and even acts on gold and platinum, but especially on the first.

Properties.

359. When its solution is poured into solutions of alkalies, or alkaline earths, or when made to act on their carbonates, triple compounds are formed of oxygen, iodine, and the metallic bases, called by Sir H. Davy *oxyiodes*; and by Gay-Lussac, perhaps more properly, *iodates*.

Produces iodates.

360. Iodic acid enters into combination with all those fluid or solid acids, which it does not decompose. All its acid combinations redden vegetable blues, dissolve gold and platinum; and when added to alkalies or earths, afford common neutral salts, and their respective iodates. H. 1. 225.

Combines with acids.

361. *Iodous Acid*. The iodous acid is prepared by triturating iodine with three parts of chlorate of potassa in a glass or porcelain mortar, until they form a very fine pulverulent yellow mass, in which the metallic lustre of the iodine is no longer perceptible. The mixture is then heated in a glass retort; and as soon as the chlorate begins to lose oxygen, the iodous acid

Iodous acid.

* The iodine may be introduced into a small flask, and the oxide of chlorine disengaged from it, upon a proper mixture of chlorate of potassa and sulphuric acid or 100 grains of chlorate of potassa may be introduced into a small retort, with 400 grains of liquid muriatic acid of the sp. gr. 1,105: annex to the retort a small globular receiver, having a bent tube issuing from it, and passing to the bottom of a small flask, containing about 50 grains of iodine; carefully apply the heat of a lamp to the retort, by which oxide of chlorine will be disengaged, and which will be decomposed and absorbed by the iodine.

† The term *anhydrous*, which will be often used, is derived from a Greek word signifying *without water*.

rises in the form of a dense white vapour, and condenses in the neck of the retort into a yellow liquid, which falls in drops into the receiver *

Properties.

362. Iodous acid is of a yellow colour; its taste acid and astringent, leaving a burning sensation on the tongue. It is of an oily consistency, and flows with difficulty. It is heavier than water, sinking in it. It has a particular odour, disagreeable, and something resembling that of euchlorine. It permanently reddens vegetable blues, but does not destroy them. It is very soluble in water and alcohol, producing amber-coloured solutions. It evaporates slowly, and entirely in the air. It is decomposed by sulphur, disengaging a little heat, and liberating violet vapours. It is characterized by the manner in which potassium and phosphorus act on it; the instant they touch it they inflame; the potassium producing a white flame and dense vapours, but little or no liberation of iodine; and the phosphorus, with a noise as of ebullition, violet vapours appearing at the same time.†

Its composition has not been experimentally ascertained.

Chloriodic acid.

363. *Iodine and Chlorine.* Iodine absorbs less than one third its weight of chlorine, and forms a peculiar acid which may be called *chloriodic acid*, and its compounds *chloriodates*. This acid is easily obtained by the direct action of chlorine upon iodine. They unite and form crystals of a deep orange colour, deliquescent, and easily fusible and soluble.‡

364. According to Gay-Lussac, indeed, two compounds result, the one of a fine orange-yellow colour, containing the largest proportion of chlorine, the other orange-red. Both are solid and crystalline; deliquescent when exposed to the air; are fusible into an orange liquid; and give an orange-coloured gas. The watery solution takes more iodine, and acquires a deep colour; but if agitated with chlorine, it is deprived of colour, and when poured, in that state, into solution of potassa, the deflagrating salt is precipitated. From liquid ammonia, the colourless liquid precipitates a white detonating compound; but the coloured solution throws down the darker compound, which detonates on the slightest touch, and is indeed, identical with that procured by the direct action of iodine on ammonia, to be hereafter described.

Precipitates metallic salts.

365. Chloriodic acid (or *chlorure of iodine*, as it is called by Gay-Lussac) precipitates the salts of iron, lead, tin and copper; probably in the state of iodates.

* The receiver should be kept cool during the whole operation.

† This acid was discovered in 1824 by Prof. Sementini of Naples—(See *Boston Journal of Philos.* ii. 292.) who obtained it from equal parts of chlorate of potassa and iodine. According to M. Wohler it is only a mixture of chloride of iodine and iodine. *Ann. Philos.* N. S. 1827.

‡ According to Davy, (*Phil. Trans.* 1814,) this compound contains 125 iodine, 36 chlorine.

SECTION VI. Of Fluorine.

366. The mineral substance called Fluor spar, or Derbyshire spar, from the place where it occurs in large quantity, is a compound of lime and a peculiar acid called the Fluoric. The experiments of Sir H. Davy led him, in 1808, to consider this acid a compound of oxygen with a peculiar base. When this acid was submitted to the action of voltaic electricity, a gas was evolved at the negative pole, which appeared to be hydrogen. The platinum wire at the opposite pole was rapidly corroded, and covered with a chocolate powder, the properties of which seem not to have been examined.*

367. When fluat of ammonia was treated with potassium no evidence was obtained of its containing oxygen. Charcoal, intensely ignited in fluoric acid gas, gave no carbonic acid. Sir H. Davy hence inferred that fluoric acid is composed of hydrogen and a peculiar base, possessing like oxygen and chlorine, a negative electrical energy and hence determined to the positive surface. For this base, which like chlorine, he believes to combine at once with metals, the name *fluorine* was proposed. H. 1,228—According to this view, fluor spar is a *fluoride* of calcium, that is, a compound of fluorine and the metallic base of lime.

368. Dr Henry makes the atom of fluorine, as deduced from the composition of fluor spar 17,1; and fluor spar a compound of 20 or 1 atom calcium + 17,1 or 1 atom fluorine. According to Dr Thomson it is 0,25 oxygen = 1 which is equivalent to 2 Hydrogen being unity.

Discovery.

Fluorides.

Atomic weight.

CHAPTER III.

OF ELECTRO POSITIVE SUBSTANCES.

369. THIS class will include all those bodies which, when separated from their combinations with the substances described in the last chapter, by voltaic electricity, are attracted by the negative surface. They are sometimes called *simple combustibles*, and subdivided into non-metallic and metallic bodies. With few exceptions, the non-metallic bodies combine with the electro-negative substances, and of the compounds formed, one or more are acids, hence they are also called *simple acidifiable* substances.

Simple combustibles.

Simple acidifiable substances not metallic.

The non-metallic substances are

Hydrogen.
Nitrogen.
Sulphur.
Phosphorus.
Carbon.
Boron.
Silicon.
Selenium.

* Phil. Trans. 1813, part 2: and 1814, part 1.

To these probably belong the bases of Zirconia, Glucina and Yttria, which have heretofore been classed with the metals; but although agreeing in several respects with metallic bodies, they are deficient in others.

SECTION I. *Hydrogen.*

370. Hydrogen was first duly examined by Mr Cavendish.* The most simple form in which it has hitherto been obtained, is in that of a gas, that is, in a state of union with caloric, and perhaps with electricity and light. From this combination we are not able to separate it, except by availing ourselves of the affinity of some other substance, in which case the hydrogen separates from the caloric, and forms with the body which has been added, a new combination. Of its nature we know but little, but as it has not yet been resolved into any more simple form, it is still arranged among elementary bodies.

Method of
procuring hy-
drogen gas.

Pl. 3.

371. To procure hydrogen gas, let sulphuric acid, previously diluted with five or six times its weight of water, be poured on iron filings, or on small iron nails; or (what is still better) pour sulphuric acid, diluted with eight parts of water, on zinc, granulated by pouring it melted into cold water, and contained in a gas bottle, fig. 65, or small retort. An effervescence will ensue, and the escaping gas may be collected in the usual manner over water.

Inflammable
air lamp.

372. An ingenious apparatus for obtaining it instantaneously, in a laboratory, is described by Gay-Lussac, in the 5th vol. of *Ann. de Chim. et Phys.* p. 300.

It consists of a three necked glass bottle, fig. 85, one of whose openings has a stopper, from which is suspended a small cylinder of zinc *a*. To the opposite aperture is fixed a bent brass tube furnished with a stop-cock, on which may be screwed either a small jet for burning the gas, or a tube to conduct it wherever it may be required. The upper vessel is of glass, and ground to fit the middle neck, its pipe reaching within a small distance of the bottom of the bottle. To use the apparatus, the lower vessel is filled with sulphuric acid properly diluted, and the zinc cylinder is then introduced, the stopper being closed to which it is affixed, and the cover of the upper vessel removed. The gas, which is generated, drives the diluted acid into the upper vessel, and the further production of it ceases, when the zinc is completely uncovered. We have then the bottle filled with gas; and can at any time expel it by opening the cock, and allowing the atmosphere to press on the surface of the liquid in the globular vessel.

Impure as
commonly
obtained.

373. Hydrogen gas, thus obtained, is not, however, to be considered as absolutely pure.† An observation of Mr Cuthbertson long ago rendered it probable, that, when disengaged

* *Phil. Trans.* vol. lvi.

† In order to purify the zinc Dr Thomson exposes it to a white heat in a stone ware retort, luted to a receiver nearly filled with water. At this temperature, the zinc is sublimed and freed from all its impurities, except a trace of cadmium too minute to occasion any sensible error. The zinc thus distilled over is melted in a crucible and poured upon the surface of a clean smooth sandstone, upon which it forms a thin sheet which can be easily broken into small pieces. *T. First Prin.* 1. 52.

by zinc, it contains a portion of that metal; and, when generated by means of iron, it is apt to contain a little carburetted hydrogen.

374. Hydrogen is an æriform fluid, but very slightly absorbable by water. It has no taste, and may be respired for a short time, though it is instantly fatal to small animals. As usually prepared it has a disagreeable odour. Berzelius has shown that the gas generated from iron filings and dilute sulphuric acid, loses its odour by being passed through pure alcohol, and when the alcohol is diluted with water and is kept a few days, an odorous volatile oil is separated, which caused the smell of the gas. Properties.

Perfectly inodorous hydrogen was obtained by Berzelius by putting an amalgam of potassium and mercury into pure distilled water; but an acid, or muriate of ammonia, added to the water, while it accelerates the formation of gas, gives it also the same odour as that remarked in the solution of zinc by diluted sulphuric acid. This odour must therefore arise from impurities.* Inodorous hydrogen.

375. It is the lightest body known, and is therefore conveniently assumed as unity in speaking of the specific gravity of gases, as well as in referring to the proportions in which bodies combine. 100 cubic inches weigh 2,118 grains. Its specific gravity is 0,0694 when common air is taken as 1,00. If oxygen is taken as unity, the specific gravity of hydrogen will be 0,0625, and 0,125 will represent its atomic weight. Weight and Specific gravity.

376. The levity of hydrogen may be proved by experiment.

Let a jar filled with this gas stand, for a few seconds, with its open mouth upwards. On letting down a candle, the gas will be found to have escaped. Exp.

Place another jar of the gas inverted, or with its mouth downwards. The gas will now be found to remain a short time in the jar, being prevented from escaping upwards by the bottom and sides of the vessel. Exp.

377. Hydrogen, in consequence of its extreme lightness, is employed for filling air-balloons.

Fill, with hydrogen gas, a bladder furnished with a stop-cock, fig. 71; and adapt to this a common tobacco-pipe. Dip the bowl of the pipe into a lather of soap, and, turning the cock, blow up the lather into bubbles, instead of falling to the ground, like those commonly blown by children, they will rise rapidly into the air. Pl. 3.
Exp.

The experiment may be varied by filling the bladder with a mixture of two parts of hydrogen gas and one of oxygen gas. Bubbles, blown with this mixture, take fire on the approach of a lighted candle, and detonate with a loud report. It is proper, however, not to set them on fire, till they are completely detached from the bowl of the pipe; otherwise the contents of the bladder will be exploded, with considerable danger to the operator. Exp.
Caution.

378. Hydrogen is inflammable, and when pure burns with a lambent blue flame at the surface in contact with the air. Inflammable.

Fill a small jar with the gas and holding it with the mouth downwards, bring the gas into contact with the flame of a candle. Exp.

Fill with this gas a bladder which is furnished with a stop-cock, and with a small pipe, of diameter less than that of a common tobacco-pipe. Press the air out through the pipe, and on presenting a lighted candle, the stream will take fire, and continue to burn with a pale and feeble flame. Exp.

* *Quart. Jour.* xvii. 380. *Ann. of Philos.* N. S. viii. 329.

Persons, who are provided with the jars represented fig. 69, *a*, may screw to the cock a brass pipe with a small aperture. On pressing the jar, filled with hydrogen gas, into the water, and opening the cock, the gas will be forced out in a stream, which may be set on fire. On this principle are founded the artificial fireworks without smell or smoke. They consist of pipes, having variously sized apertures, some of which have a rotary motion. H. 1. 233.

Döbereiner's hydrogen lamp.

379. It has been found by Prof. Döbereiner, that when a stream of hydrogen is directed upon spongy platinum (obtained by adding muriate of ammonia to a solution of platinum in nitromuriatic acid) the platinum soon becomes red hot, and the hydrogen is inflamed.*

Pl. 2.

This discovery has led to various modifications of the inflammable air lamp (372). A very convenient and ornamental form of which is represented in fig. 86. It is composed of two glass vessels fitted to each other by grinding, as in the apparatus of Gay-Lussac. The tube *a*, of the upper vessel is encompassed by a cylinder of zinc, which is supported by a ring of cork on the lower part of the tube. The platinum sponge is contained in a small brass box *b*, attached to a brass wire passing through a collar of leather and which can be placed at any distance from the jet, *c*. When a light is required the cock *d* is turned, and the pressure of the acid liquor in the upper vessel expels the hydrogen, as in the apparatus already described.†

Pl. iv.

Detonates with air.

380. If mixed with common air, hydrogen burns rapidly with detonation.

Into a strong phial, capable of holding about 6 ounces of water, introduce one part of hydrogen and three parts of common air. On applying a lighted candle or a red hot wire, the mixture will explode.

Inflammable air pistol.

This experiment may be performed by means of an apparatus called the inflammable air pistol, fig. 87. This instrument consists of a cylinder of brass, about three-fourths of an inch diameter, and six inches long, in the form of a small cannon or pistol-barrel, properly mounted, and having a wire, *a*, passing through a tube of ivory, *b*, and not quite touching the interior of the cylinder, at the part usually occupied by the touch-hole; an electric spark communicated to this wire inflames the mixture of hydrogen and atmospheric air in its interior. It may be charged by previously filling it with dry sand, and emptying it out into a phial of hydrogen, which rises into the gun sufficiently mixed with air; the muzzle may be secured by a cork, which is expelled with much violence and a loud report, upon the inflammation of the gas. It may be also charged, by holding it for a moment over the open jet of the instrument, fig. 85, always taking care that there is a due admixture of atmospheric air, otherwise the electric spark will not inflame it.

Detonates with oxygen,

381. If the experiment be repeated with oxygen gas instead of atmospherical air; changing the proportions, and mixing only one part of the oxygen gas with two of hydrogen, the report will be considerably louder. The bottle should be a strong one, and should be wrapped round with cloth, to prevent an accident.

and by means of the electric spark.

The same experiment may be made over water, by means of the electric spark. Procure a strong tube, about three quarters of an inch diameter, and 12 inches long, closed at one end, fig. 88. About a quarter or half an inch from the sealed end, let two small holes be drilled, opposite to each other, and into each

Pl. 4.

* A convenient tinder may be prepared from a piece of cotton cloth dipped in the solution and then inflamed, it ignites as readily as the platinum sponge; the sponge and tinder should be perfectly dry. W.

† See the subject of *Eudiometry*.

of these let a brass conductor be cemented, so that the two points may be distant from each other, within the tube, about one eighth of an inch. An apparatus, serving the same purpose, and much more easily constructed, may be formed by hermetically sealing a piece of brass wire, or still better, platinum wire, into the end of a glass tube. With this conductor, an interrupted circuit may be formed by introducing into the tube a longer wire, one end of which terminates one-tenth of an inch from the upper one, while the other extends beyond the aperture of the tube. (See fig. 77, c.) Into this tube, standing over water, pass about half a cubic inch of a mixture of hydrogen and oxygen gases; in the proportion of two measures of the former to one of the latter. Hold the tube firmly, and pass an electric spark through the mixed gases. For relieving the shock, which is sometimes considerable on firing, an ingenious contrivance of Sir H. Davy may be employed.* The first effect of the combustion is a sudden and considerable enlargement of volume, which from some experiments of Sir H. Davy (on *Flame*, p. 90) probably amounts to 15 times the original bulk of the mixture. After this the gases if perfectly pure, and in the proper proportion, will be found to have disappeared entirely. H. 1. 235.

Pl. 3.

382. A current of hydrogen may be inflamed when issuing from a small aperture, and if a tube of 18 or 20 inches in length be held over the flame, a peculiar musical tone is produced. This effect is not peculiar to hydrogen, but is produced by a variety of other flames, and is referable to the succession of explosions produced by the combustion of the gas in the tube.†

Musical tones during the combustion of hydrogen.

Bring an inverted jar, filled with this gas, over the flame of a candle; and suddenly depress the jar, so that the lighted wick may be wholly surrounded by the gas. The candle will immediately be extinguished.

Does not support combustion.

Fill a small jar with hydrogen, and having covered its mouth with a card bring it with its mouth downwards near a lighted candle; holding the mouth on a level with the flame, remove the card and depress the jar over the flame; the candle will be extinguished but the hydrogen will continue to burn at the mouth of the jar, on slowly raising the jar the candle will be relighted as it passes through the burning gas—on depressing the jar the candle will be again extinguished, and may be relighted as before. W.

Exp.

383. The tendency which gaseous fluids have to become completely mixed under all circumstances, and as it were to penetrate each other, is well illustrated where hydrogen is employed. Thus, if two small phials, the one containing oxygen and the other hydrogen, be connected perpendicularly by a long glass tube, of small bore, it will be found, that although the hydrogen be uppermost, and much lighter than the oxygen, it will, in the course of a few hours, have perfectly mixed with the oxygen, and the gases will be found in equal proportions in

Gases have a powerful tendency to mix together.

Exp.

* *Philos. Magazine*, xxxi. 3.† Faraday, *Journal of Science and the Arts*, vol. v.

both phials. Mr Dalton has shown that gases, unlike other fluids, do not remain upon each other without admixture.*

Dr Hare's
blow pipe.

Pl. iv.

384. The flame of hydrogen is occasionally employed for exciting intense heat; and it has been found when mixed with oxygen and burned as the mixture issues from a small jet, to excite a temperature nearly equal to that of the arc of flame in the Voltaic circuit. A blow pipe upon this construction was first made by Professor Hare of Philadelphia; it consists of a cylindrical vessel of tin, fig. 89, *a*, or what is preferable copper, divided in the middle by two partitions, so as to form two distinct reservoirs, one for oxygen and the other for hydrogen. Into the lower part of each reservoir a tube *b*, is inserted somewhat obliquely, as in the common gas holder. Above the reservoirs is a conical tin funnel *c*, furnished with a stop-cock and connected with a tube which immediately below divides into two, one passing to each reservoir. A tube passes out from each reservoir, which meet in a cone *d* (a section of which is represented at *e*). The gases are thus mingled and are then made to issue through a capillary tube drilled through a wire of silver and inserted into the cone.† The lower tubes being closed, the apparatus is filled with water, and the gases introduced, as in the usual method of filling a gas holder. The reservoirs being filled, the lower tubes are closed, and water poured into the funnel, on opening the stop-cocks the gases are propelled through the jet. When substances are to be exposed to the action of this instrument, the stop-cock connected with the reservoir of hydrogen should be first opened and the gas may be inflamed; the other stop-cock is then gradually opened, and the oxygen mixing with the hydrogen, an intensely high temperature is obtained.

With this instrument Professors Hare and Silliman first effected the fusion of some of the most refractory substances in nature.‡

Brooke's
blow pipe.

385. The blow pipe invented by Mr Brooke§ depends for its action on the elasticity of compressed air, and consists of a strong copper box, fig. 90, into which several atmospheres are crowded by means of a condensing syringe. Various expedients have been adopted to render this a safe substitute for the oxyhydrogen blow pipe of Dr Hare. The most effectual of which consists in interposing between the flame and the main reservoir of gases, a cylinder containing a little water or oil, through which, by means of a valve at the bottom, the gases are allowed to pass. The safety of the instrument is increased by the inter-

* *Manchester Memoirs*, vol. i. New Series.

† The arrangement represented Pl. ix fig. 27, consisting of two reservoirs for the gases is perfectly safe and convenient: the jet may be formed of two concentric cones, fig. 16.

‡ *Amer. Jour. of Science*, vol. ii. p. 281, &c.

§ The invention of this blow pipe is often ascribed to Dr Clarke, but is due to Mr Brooke, by whom it was exhibited to the compiler before it was made public. W.

position of a bundle of capillary tubes, between the stop-cock and the orifice of the pipe at which the gases are inflamed.*

Mr Skidmore of New York has discovered that the flame produced by the oxyhydrogen blow-pipe continues to burn when submersed in and in actual contact with water, with the same splendour as in the atmosphere; the only difference being that under water, its figure is conglobated, whereas in air it assumes that of a long slender conical pencil. Care is required to introduce the flame slowly into the water. A piece of pine wood or cork when brought within the action of the submerged flame gives out a brilliant light.†

Burns under water.

386. *Hydrogen and oxygen*.—When two volumes of hydrogen gas are mixed with one volume of oxygen gas, and the mixture inflamed in a proper apparatus by the electric spark, the gases totally disappear, and the interior of the vessel is covered with drops of pure water, equal in weight to that of the gases consumed.

Union with oxygen gas, produces water.

387. If pure water be exposed to the action of Voltaic electricity, it is resolved into two volumes of hydrogen, disengaged at the negative pole, and one volume of oxygen, disengaged at the positive; (235) so that water is thus proved by synthesis and analysis, to consist of two volumes of hydrogen combined with one volume of oxygen.

Composition of water.

388. In determining the proportion of the elements of water, every thing will depend on the precision with which the specific gravities of oxygen and hydrogen gases are ascertained. According to the results of Dr Thomson, oxygen gas is precisely 16 times heavier than hydrogen gas, and according to Berzelius and Dulong a very little more than 16 times; but if we take 16 to 1 as the nearest approximation, it will follow, since water consists of two volumes of hydrogen and one of oxygen, that eight parts by weight of oxygen and one of hydrogen constitute water; or according to the last mentioned chemists it consists of

| | |
|--------------------|-----------------|
| Oxygen | 88,9 |
| Hydrogen | 11,1 |
| | <hr/> |
| | 100. H. 1. 250. |

* In the blow-pipe of Mr Gurney the mixed gases are contained in a silk bag, or bladder, fig. 91, *d*, which is supported on a table *l, l, l*, and the necessary degree of pressure is obtained by weights or by the hand upon a moveable press board *m*, below. The gases are conveyed to the bag by means of a pipe laid into and across the table furnished with a stop-cock *h*, upon which may be screwed the bag *g*, or a tube connected with a gas holder. By this arrangement the apparatus may be kept in action for any length of time. Between the reservoir *d*, and the stop-cock *h*, a valve is placed to prevent the return of the gases when pressure is applied at *m*; *i, i*, is a light pasteboard or wood cap which in case of an explosion of the gazometer is thrown into the air, by the force rupturing the strings *k, k, k, k*, which, from its extent of surface and great lightness is arrested by the atmosphere. To the stop-cock *c*, a safety apparatus *b*, is attached, which is filled with water to the height *b*, and the gases pass from the reservoir *d*, through a tube reaching to the bottom of the vessel; the upper part of which is closed by a cork *e*; in case of an explosion of the small quantity of gas above the surface of the water, the cork is thrown up; additional security is obtained by a small chamber *a*, containing layers of wire gauze. For a more particular description of this blow pipe, see Gurney's *Lectures*, p. 288.

Gurney's blow-pipe.
Pl. iv.

† Amer. Jour. of Science, v. 347.

And if water be constituted of one atom of oxygen united with one atom of hydrogen, if we represent the weight of the latter by 1, that of the atom of oxygen will be 8, and $1 + 8 = 9$ is the representative number for water. Or thus

| | | |
|-----------|---------|-------|
| Hydrogen. | Oxygen. | Water |
| 1 | 8 | 9 |

If we assume the weight of oxygen as 1, hydrogen will be 0,125, and the representative number of water 1,125. If we conceive that water is composed of two atoms of hydrogen and one of oxygen, we must double the number for oxygen, in which case we should have 17 for the representative number for water.

But it admits of being proved to be consistent with mechanical principles that the most energetic combination of any two elements is that in which they are united particle to particle. Until therefore the contrary can be established, we may assume, with Mr Dalton, that water is a binary compound of 1 atom of oxygen, and 1 atom of hydrogen. H. 1. 249.

389. The experiments illustrating the composition of water may be divided into synthetic and analytic. Among these the following may be selected.

Pl. iv.

Exp.

Burns with oxygen gas and forms water.

Burn a current of hydrogen under the funnel *a*, fig. 92; by uniting with the oxygen of the atmosphere it will produce aqueous vapour, which passing into the glass cylinder *b*, will condense in drops.

Fig. 93, represents an apparatus for showing the production of water by burning a current of hydrogen in an atmosphere of oxygen. *a* is a glass cylinder, which after having been exhausted upon an air-pump, is filled with pure oxygen. *b* is a receiver of hydrogen immersed in the vessel of water *c*, by which the gas is compressed, so as to be urged through the capillary opening *f*, when the stop-cocks *d d* are open. *e* is a platinum wire by which the gas may be inflamed by an electric spark. It burns with the production of intense heat, and water is soon collected in drops upon the interior of the cylinder.

The mixture explodes.

Exp.

If two measures of pure hydrogen be mixed with one of pure oxygen, and detonated in the graduated glass tube *a*, fig. 88, standing over water, by an electric spark passed through the platinum wires *b b*, the gases will entirely disappear. If there be any excess of either of the gases, the portion in excess will remain unconsumed.

Exp.

The same experiment may be thus varied, fig. 94, is a very strong glass vessel, capable of holding about half a pint and furnished (besides the proper contrivance at top for taking the electric spark in it) with a brass cap and cock, by means of which it can be screwed to the transfer plate of an air-pump. When exhausted, it may be filled with a mixture of oxygen and hydrogen gases, in the proportion of one measure of the former to two of the latter, and an electric spark may be passed through the mixture. After the explosion, when time has been given to the vessel to cool, a sensible quantity of moisture will have condensed on the inner surface of the vessel, and by repeating the operation frequently, a sufficient quantity of fluid may be collected to show that water is the only product.

390. The water produced in this mode, is not, however, to be considered as a compound of the two gases, but only of their bases, for the light and caloric, which constituted the gases, escape, in considerable part during the combustion. Every gas, it must be remembered, has at least two ingredients; the one, gravitating matter, which, if separated, would probably exist in a solid or liquid form; the other, an extremely subtle fluid, termed caloric and perhaps electricity and light. The compound, water, is therefore said to be composed of hydrogen and oxygen, the *bases* of the gases, and not of hydrogen and oxygen *gases*.

Water a compound of the bases of the gases.

391. Water may be decomposed or resolved into its elements by a variety of processes, the most important of which are the following:

Analysis of water,

Fig. 95, *a* is a glass retort, into which is introduced a given weight of water; *b b*, a small furnace through which passes the earthen, or iron, tube *c c*, which terminates in the spiral pewter tube *d d*, immersed in water. A given weight of pure iron coiled up, is introduced into the tube *c*, and the whole made red hot; the water in *a* is then made to boil, and the vapour, on coming into contact with the red hot iron, is in part decomposed; the oxygen is retained by the iron, and the hydrogen escaping through the tube *f*, may be collected as usual. Any undecomposed portion of water is condensed in the worm-pipe *d*, and drops into the vessel *e*.

Pl. iv.
by iron,
Exp.

After this experiment the iron will be found to have increased in weight; and if attention be paid to the quantity of water which has collected in *e*, and to the weight of the hydrogen gas evolved, it will be found that the weight gained by the iron, added to that of the hydrogen, will be equal to the weight of the water which has disappeared. Lavoisier concluded, from an experiment thus conducted, that water consists of 85 *per cent.* by weight of oxygen, and 15 by weight of hydrogen; that is, that for every 15 grains of hydrogen evolved, 85 grains of oxygen were condensed by the iron.

392. The processes, by which the elementary parts of water are separated from each other, and are *both* obtained in an *aëri-form* state, as a mixture of hydrogen and oxygen gases, are dependent on the agency of electricity.

The first of these experiments requires for its performance the aid of a powerful electrical machine. This fact was the discovery of a society of Dutch chemists; and the principal circumstance, in the experiment, is the transmission of electrical shocks through a confined portion of water. The apparatus employed, in this experiment of Messrs Dieman and Van Troostwyk, is a glass tube, about one-8th of an inch diameter, and 12 inches long, one of the ends of which is sealed hermetically, a gold wire being inserted at this end, and projecting about an inch and a half within the tube. About the distance of five-8ths of an inch from the extremity of this, another wire is to be fixed, which may extend to the open end of the tube. The tube is next to be filled with distilled water, and to be placed inverted in a vessel of the same. When thus disposed, electrical shocks are to be passed between the two ends of the

by Electricity,

wire, through the water; and, if these shocks be sufficiently strong, bubbles of air will be formed at each explosion, and will ascend till the upper part of the wire is uncovered by the water. As soon as this is effected, the next shock that is passed will set fire to the mixed gases, and the water will rise again in the tube, a very small quantity of gas remaining. Now, as hydrogen and oxygen gases, in a state of admixture, are capable of being inflamed by the electric shock, and as there is nothing in the tube, beside water, that can afford them in this experiment, we may safely infer, that the evolved hydrogen and oxygen gases arise from decomposed water.

by Voltaic
electricity,

Pl. iv.

393. The decomposition of water by galvanic electricity is a process singularly adapted to demonstrate the fact in a simple and elegant manner, since it exhibits both the oxygen and hydrogen in the gaseous form. Fig. 96, represents a section of an apparatus for this purpose. It is a glass vessel containing water, having two wires of platinum, *a a*, passing through its bottom: over these are inverted the tubes *b b*, also filled with water. The wires are rendered positive and negative by connexion with a moderately powerful Voltaic apparatus. Oxygen is evolved at the positive wire, and hydrogen at the negative wire, which gases rise into the tubes, and it is seen that one volume of oxygen, *o*, and two volumes of hydrogen, *h*, are the constant results. If these gases be mixed and detonated, pure water is again formed.

by living
vegetables.

Exp.

394. Another mode of effecting the decomposition of water yet remains to be mentioned, in which, not the hydrogen, but the oxygen is obtained in a gaseous state. This is by the action of living vegetables, either entire or by means of their leaves only. Fill a clear glass globe with water, and put into it a number of green leaves, from almost any tree or plant. A sprig or two of mint will answer the purpose perfectly well. Invert the glass, or place it, with its mouth downwards, in a vessel of water. Expose the whole apparatus to the direct light of the sun, which will then fall on the leaves surrounded by water. Bubbles of air will soon begin to form on the leaves, and will increase in size, till at last they rise to the top of the vessel. This process may be carried on as long as the vegetable continues healthy; and the gas, when examined, will prove to be oxygen gas, nearly pure. In this experiment, the hydrogen combines with the plant, to the nourishment and support of which it contributes, while the oxygen is set at liberty. H. 1. 253.

395. Water, in its ordinary state, such as spring and river water, is always so far contaminated with foreign substances as to be unfit for many chemical purposes, and frequently, as will be more fully shown hereafter, even for domestic use. Rain-water is much more pure, but it always contains a portion of carbonic acid and of the elements of atmospheric air, besides appreciable traces of vegetable or animal matter; to the latter it

owes its property of becoming putrid when kept. The distinction of water into hard and soft has reference to its less or greater purity. The impurities of water are separated by distillation.*

Heterogeneous contents.

396. *Distilled Water*, as commonly prepared, always affords minute traces of foreign matter, especially when subjected to Voltaic decomposition, and can only be considered as perfectly pure when re-distilled at a low temperature in silver vessels.

397. Pure water is transparent, and without either colour, taste or smell. In consequence of the facility of obtaining it pure, it is assumed as a standard to which the relative weight of all other bodies may be compared, its specific gravity being called = 1,000, and hence the importance of estimating its weight with precision. At the temperature of 40° it is at its maximum of density, and at that temperature an English cubic foot weighs 437102,4946 grains,† or 999,0914161 ounces avoirdupois, and the cubic inch 252,953 grains.‡

Properties.

Standard of specific gravity.

398. At the temperature of 32° water congeals into ice, which, if slowly formed, produces needles crossing each other at angles of 60° and 120°. The specific gravity of ice is 0,94. Exposed to the air, ice loses considerably in weight by evaporation.

Ice.

399. If water be exposed to heat in open vessels it boils or is converted into steam, at 212°, the barometer being at 30 inches; but the boiling point of water varies considerably with the pressure (157.) The specific gravity of air being considered as = 1; that of steam is 0,625. At mean pressure, and at the temperature of 212°, the bulk of steam is 1700 times greater than that of water.

Boiling point.

400. Water is susceptible of compression, as was originally shown by Canton, and more lately by Mr Perkins, who has estimated, in an ingenious series of experiments, the rate of its compression.§ If submitted to very sudden compression, water becomes luminous, as has been shown by M. Desaignes.|| According to M. Despretz the compression of water by a force equal to 20 atmospheres, causes the evolution of $\frac{1}{66}$ th part of a degree of heat.

Compressible.

401. Water enters into combination with a variety of substances, and is retained with various degrees of force. Sometimes it is contained in a variable ratio, as in ordinary solution;

State of combination.

* This process is usually conducted upon the large scale in a copper boiler, fig. 97, placed either in a portable furnace, or set in brickwork, according to its dimensions, to which is annexed a head, *b*, of the same material, or of pewter, connected with a spiral tube or worm, which is immersed in the worm-tub, or refrigerator *d*, its lower end passing out. The water in the worm-tub must always be retained of a low temperature to effect the condensation of the vapour in the spiral tube.

Pl. iv.

† Thomson's *System*, vol. ii. p. 18.

‡ According to the late parliamentary standard of Great Britain, the pint of water consists of 8750 grains of water at 62° F. barometer at 30 inches, and the cubic inch of 252,458 grains. The gallon contains 277,274 cubic inches, or 70,000 grains of distilled water; the pint 34,65925 inches or 8750 grains.

§ *Phil. Trans.* 1820.

|| Thonard, *Traité de Chimie*, i. 432.

in other compounds it is present in a fixed definite proportion, as in its union with several of the acids, the alkalies, and all salts that contain water of crystallization. These combinations are termed *hydrates*; thus the strongest liquid of sulphuric acid is a compound of one atom of the real dry acid and one atom of water; and its proper name is *hydrous sulphuric acid*, or *hydrate of sulphuric acid*.

Hydrates.

Water contains air.

402. Water, which has been exposed to the atmosphere, always contains a portion of air, as may be proved by boiling it, or by exposing it under the exhausted receiver of the air-pump. To separate the air, the water must be boiled for about two hours. It absorbs oxygen gas in preference to atmospheric air or nitrogen, and when the air is expelled by boiling, the last portions contain more oxygen than those first given off.*

Absorption of gases by water.

403. Every gas is absorbed by water, which has been deprived of all or the greatest part of its air by long boiling. The quantity, however, which water is capable of absorbing, varies considerably with respect to the different gases. Those gases, of which only a small proportion is absorbed, require violent and long continued agitation in contact with water. H. 1. 253. In the common process of manufacturing soda water a large quantity of carbonic acid gas is absorbed by the water, and an additional portion is mechanically united with it by powerful compression.†

Hydrogen assumed as unity.

404. As hydrogen is the lightest known substance, it is assumed, as already remarked (87), by many chemists as *unity*, in reference to the representative numbers of other bodies. The principle of numeric representation, or of equivalent or proportional numbers, has been adverted to (75, &c.) and the following will be the representative numbers of some of the bodies described in the foregoing sections, the number for oxygen being deduced from the composition of water (348), and of chlorine and iodine from the muriatic and hydriodic acids.

| Undecomposed Substances. | Proportional numbers. |
|--------------------------|-----------------------|
| Hydrogen | 1 |
| Oxygen | 8 |
| Chlorine | 36 |
| Iodine | 125 |

* Humboldt and Gay-Lussac, *Journal de Physique*, 1805.

† The following table from Dr Henry's chemistry shews the absorbability of different gases by water deprived of all its air by ebullition.

100 cubic inches of such water, at the mean temperature and pressure, absorb of

| | Dalton and Henry. | Saussure. |
|-----------------------|-------------------|-----------|
| Sulphuretted hydrogen | 100 cubic inches | 253 |
| Carbonic acid | 100 " " | 106 |
| Nitrous oxide | 100 " " | 76 |
| Olefant gas | 12.5 " " | 15.3 |
| Oxygen | 3.7 " " | 6.5 |
| Carbonic oxide | 1.56 " " | 6.2 |
| Nitrogen | 1.56 " " | 4.1 |
| Hydrogen | 1.56 " " | 4.6 |

The estimate of Saussure is in general too high. That of Mr Dalton and Dr Henry for nitrous oxide is considerably beyond the truth, according to the experiments of Sir H. Davy.

| Compounds. | Component Parts. | Representative Numbers. |
|----------------------|---|-------------------------|
| Water | { 1 proportional of hydrogen = 1 ditto oxygen = | 1 } 9. |
| Peroxide of chlorine | { 4 proportionals of oxygen = 1 ditto chlorine = | 32 } 68. |
| Chloric acid | { 5 proportionals of oxygen = 1 ditto chlorine = | 40 } 76. |
| Perchloric acid | { 7 proportionals of oxygen = 1 ditto chlorine = | 56 } 92. |
| Iodic acid | { 5 proportionals of oxygen = 1 ditto iodine = | 40 } 165. |
| Chloriodic acid | { 2 proportionals of chlorine = 1 ditto iodine = | 72 } 197. |

405. *Deutoxide* or *Peroxide of Hydrogen*.—M. Thenard Peroxide of hydrogen. has shown that water may be united to a considerable excess of oxygen by means of peroxide of barium.* This new compound is possessed of very remarkable properties.†

The peroxide of hydrogen has a specific gravity of about 1,452 and is a colourless transparent liquid without odour. It acts as a caustic upon the skin, thickens the saliva, and tastes like certain metallic solutions. It destroys the colour of litmus and turmeric paper. It continues liquid at all degrees of cold to which it has hitherto been exposed. At the temperature of 59° F. it is decomposed, being converted into water and oxygen gas. Properties.

406. The peroxide of hydrogen is decomposed with remarkable facility. The diffused day-light does not seem to exert any influence over it, and even the direct solar rays act upon it tardily. It effervesces from the escape of oxygen at 59° F. and the sudden application of a higher temperature, as of 212° F. gives rise to such a rapid evolution of gas as to cause an explosion. Decomposed with facility.

407. All the metals except iron, tin, antimony and tellurium, have a tendency to decompose the peroxide of hydrogen, converting it into oxygen and water. The decomposition is most rapid when the metals have been previously reduced to a state of minute division. The metals which have a strong affinity for oxygen are at the same time oxidized. Action of metals,

408. The peroxide of hydrogen is decomposed at common temperatures by many of the metallic oxides. of oxides,

409. Acids have the property of rendering this substance more stable : of acids.

Let a portion of the liquid, somewhat diluted with water, be heated till it begins to effervesce from the escape of oxygen gas; drop into it some strong acid, as the nitric, sulphuric, or muriatic, the effervescence will immediately cease. Exp.

* *Quart. Jour.* v. viii. p. 114.

† To obtain this product, it is necessary to employ a substance, the *peroxide of Barium*, which will be described in the section on *Barium*.

Exp. When a little gold in a state of fine division is put into a weak solution of the peroxide of hydrogen, containing only 10, 20 or 30 times its bulk of oxygen, a brisk effervescence ensues; but on letting one drop of sulphuric acid fall into it, the effervescence ceases instantly: it is reproduced by the addition of potassa, and is again arrested by adding a second portion of acid.*

Analysis. 410. The peroxide of hydrogen was analyzed by diluting a known weight of it with water, and then decomposing it by boiling the solution. From two analyses 864 parts of the peroxide are composed of 466 water, and 393 oxygen gas. The 496 of water contain 414 oxygen, whence it may be inferred that the peroxide of hydrogen contains twice as much oxygen as water. T. If water then be a compound of 1 atom of hydrogen and 1 atom of oxygen, the peroxide must consist of 1 atom hydrogen + 2 atoms of oxygen and its representative number will be 17.

Muriatic acid gas. 411. *Hydrogen and Chlorine*.—When equal volumes of these gases are mixed and exposed to light, they combine and produce a sour compound commonly called *muriatic acid gas*; or in conformity to more modern nomenclature *hydrochloric acid gas*.

412. Chlorine and hydrogen gases act with considerable energy upon each other, and with different phenomena accordingly as the experiment is conducted.

Exp. If a phial be entirely filled with a mixture of hydrogen and chlorine gases in equal proportions, and a well ground stopper be introduced; no action takes place, provided light be carefully and completely excluded, even by standing some time; but on applying a lighted taper, the gases immediately explode. H. 1. 266.

Exp. Into a small but strong vessel, guarded from the light, introduce equal volumes of the two gases, and inflame the mixture by the electric spark, muriatic gas results. The apparatus shown at fig. 94, may be used for this purpose. The vessel should be previously exhausted by the air pump, and then filled with the mixed gases. An electric spark may now be passed through the mixture, when a detonation will ensue, to avoid any injury from which, the vessel should be wrapped in several folds of cloth. If the cock, attached to the vessel, be opened under mercury in about a quarter of an hour, very little of that fluid will enter, proving that the volume of gas after the experiment is scarcely diminished; that it is diminished at all, is owing to a small portion of air being mingled with the other gases: and it was found by Sir H. Davy that the more perfectly this is excluded, the less is the amount of the contraction of volume. If the cock be now opened under water, and left there for a few minutes, the water will be found to have ascended and entirely filled the vessel. Hence a gas must have been gene-

Pl. 4.

* The only acids that do not possess this property are those that have a lower degree of acidity, as the carbonic and boracic acids; or those which suffer a chemical change when mixed with the peroxide of hydrogen.

rated by the combustion, which, though not absorbable by mercury, is condensable by water.

413. If a phial containing the mixed gases be exposed to the sun's rays a detonation will ensue, which will probably drive out the stopper. But if this should not happen the stopper may be removed under water, which will ascend and completely fill the phial as in the former experiment. Exp.
Effect of
light.

The agency of light may be beautifully shewn by filling a tube about half an inch diameter, and 12 inches long, with the mixed gases, and alternately shading it with an opaque cover, and exposing it to the sun's rays. The moment the tube is exposed even to the diffused light of day, a cloudiness will appear within it, and the water will ascend more or less rapidly according to the intensity of the light. The effect even of a passing cloud is distinctly seen in retarding the rapidity of the combination, which is very striking in the full solar light. Exp.

414. It had been supposed that the direct beams of the sun were necessary to explode a mixture of chlorine and hydrogen gases; but Professor Silliman has related the accidental explosion of a mixture of the gases, in the quantity that filled a Florence oil flask, not only when no direct solar light fell upon it, but when the diffuse light of day was rendered more feeble than common by a thick snow-storm.* This fact furnishes a caution against mixing the two gases in considerable quantities. H. 1. 268.

415. The intense light issuing from charcoal points connected with a powerful galvanic battery has been found by Mr Brande, as effectual as solar light in acting on hydrogen and chlorine gases; showing a curious analogy between electric and solar light; for ordinary artificial light does not accelerate the combination.† Effect of Voltaic Electricity.

416. When one volume of hydrogen gas has been made to combine, either silently or explosively, with one volume of chlorine, the product is two volumes of a new gas, *Muriatic Acid*, differing essentially from either of its components, and especially in being instantly absorbed by water. To preserve it, therefore, in a gaseous state, it is necessary to confine it by quicksilver. Muriatic acid gas.

417. At all common temperatures and pressures, it is permanent in this form; but it was generated by Mr Faraday in close tubes, from muriate of ammonia and sulphuric acid, in a liquid state. Its refractive power was then found equal to that of liquid nitrous oxide, but inferior to that of water. The pressure of its vapour at 50° F. was equal to about 40 atmospheres. H. 268. Liquid:

418. To obtain muriatic acid gas in sufficient quantity for the exhibition of its properties, the direct combination of chlorine and hydrogen gases is not an eligible process. It may be procured much more conveniently in the following manner. Process for obtaining.

Let the tubulated gas bottle, fig. 98, *a*, be about one fourth, or one third, filled with well dried chloride of sodium, (common Pl. 4:

* See *Amer. Jour. of Science*. iii. 342.

† Brande, *Phil. Trans.* 1820.

salt) in lumps, not in powder. To this adapt the acid holder, *b*, filled with concentrated sulphuric acid; and let the aperture of the bent pipe *c*, terminate under a jar filled with, and inverted in, quicksilver. Open the communication between the acid and the salt, by turning the cock, *d*; and immediately on the contact of these two bodies, an immense quantity of muriatic acid gas, will be disengaged. A common or tubulated gas bottle, or tubulated retort will answer sufficiently well for procuring the gas. The first portions that come over, may be allowed to escape under a chimney; because they are contaminated by the admixture of common air present in the bottle. The subsequent portions may be preserved for use. This gas was first obtained pure by Dr Priestley, but its composition was discovered by Scheele, and has since been most ably investigated by Sir H. Davy.

Properties.

419. Muriatic acid gas has a very pungent smell; and is sufficiently caustic to blister the skin, when applied to it for some time. When brought into contact with common air, it occasions a white cloud. This is owing to its union with the aqueous vapour, which is always present in the atmosphere.

Exp.

Exp.

420. It extinguishes a lighted candle. Before the flame goes out, the upper part of it assumes a greenish hue. A white vapour also surrounds the extinguished wick, owing to the combination of water, produced by the combustion of the candle, with the muriatic acid gas.

421. Muriatic acid gas is greedily absorbed by water, which at 40° F. Sir H. Davy found to take up about 480 times its bulk, forming a solution of specific gravity 1,2109.*

Exp.

Fill a narrow jar, or tube closed at one end, with muriatic acid gas, over mercury, and through the latter pass up a few drops of water, the gas will be rapidly absorbed, and the mercury will rise in the vessel.

Exp.

Into a similar vessel filled with the gas introduce a piece of ice; it will be liquefied, almost as rapidly as if touched with a red hot iron, and the gas will be absorbed.

Specific gravity.

422. It is heavier than common air. Its specific gravity, air = 1, is 1,28472 and 100 cubic inches weigh 39,1839. Its specific gravity, oxygen, = 1, is 1,15625, T; compared with hydrogen it is = 18,5.

Analysis.

423. Muriatic acid gas may be decomposed by the action of several of the metals. Potassium, for instance, absorbs the chlorine and one third its volume of hydrogen is evolved. Heated zinc and tin disengage a volume of hydrogen equal to one half that of the muriatic acid gas, and chlorides of those metals are obtained.†

When a mixture of oxygen and muriatic acid gases is either electrized or transmitted through a red hot porcelain tube, the oxygen unites with the hydrogen of the acid, and the chlorine of the latter is set at liberty. A similar mixture, Dr Henry finds, is also decomposed by being exposed, at a temperature

* Elements, p. 252.

† Davy, *Phil. Trans.* 1810.

of 250° F. to contact with the platinum sponge. Water is formed and the disengaged chlorine acts on the mercury used to confine the gas.* H. 1,268.

424. As the specific gravity of hydrogen to chlorine is as 1 Composition:
to 36,0, muriatic acid will consist of 1 hydrogen + 36,0 chlorine, and its representative number will be 37,0.

| | | | |
|----------|----------|---|---------------|
| Hydrogen | Chlorine | = | Muriatic Acid |
| 1, | 36, | | 37,0 |

When oxygen is taken as the unit, the atomic weight of muriatic acid is 4,625.

425. It is in the state of watery combination that muriatic acid is kept for chemical purposes, and all the processes for preparing the liquid acid have for their object the disengagement of muriatic acid gas, and its absorption by water. Liquid muriatic acid, how obtained.

426. For saturating water with this gas we commonly employ Woulfe's apparatus. The retort being furnished with the bent tube, *a*, fig. 23, and placed in a sand bath. The junctures should be carefully luted, and the acid should be added to the salt in the retort at intervals. The water employed may amount to half the weight of the salt, and may be equally distributed between the bottles. These it is better to surround with cold water, or, still preferably, with ice or snow; because the condensation of the gas evolves considerable heat, which prevents the water from attaining its full impregnation. When the whole of the sulphuric acid has been added, and the gas no longer issues, let a fire be lighted in the furnace, beneath the sand bath, removing the bent tube *a*, and substituting a well ground glass stopper. This will renew the production of gas; and the temperature must be preserved, as long as gas continues to be evolved. At this period it is necessary to keep the luting which connects the retort and receiver, perfectly cool.† Towards the close of the process, a dark-coloured liquid is condensed in the first receiver, consisting of a mixture of sulphuric and muriatic acids. When nothing more comes over, the operation may be suspended, and the liquid in the two receivers must be preserved in bottles with ground stoppers. It consists of liquid muriatic, or hydrochloric acid. H. 272. Pl. 1.

427. It was usual to explain the phenomena which are observed in these processes, by saying that the sulphuric acid, by its superior affinity, aided by heat, expelled the muriatic acid gas from the salt and united with its soda. The discoveries of Sir H. Davy have taught us that common salt (improperly termed *muriate of soda*, since it neither contains muriatic acid nor soda) is a binary compound of chlorine and sodium in the proportions of 36 parts of the former to 24 of the latter. Sulphuric acid is a compound of 40 parts of dry acid and 9 of wa- Davy's Theory.

* Phil. Trans. 1824.

† The clay and sand lute is the best for this juncture.

ter, which water is composed of 8 of oxygen and 1 of hydrogen; and when sulphuric acid acts upon common salt, this portion of water is decomposed; its hydrogen combines with the chlorine to form muriatic acid, and its oxygen transferred to the sodium forms soda, which unites with the dry sulphuric acid to form sulphate of soda. These decompositions are further shown in the following table.*

| | | | |
|---------------------------------|----------------|---------------|---|
| 37 Muriatic Acid | | | |
| Common Salt 60 | Chlorine 36 | Hydrogen 1 | Water 9 + Dry Sulphuric Acid 40 49 Liquid Sulphuric Acid |
| | | | |
| | Sodium 24 | Oxygen 8 | |
| | | | |
| 32 Soda + 40 Dry Sulphuric Acid | | | |
| 72 Sulphate of Soda | | | |

Properties.

428. When muriatic acid is thus dissolved in water, it forms the *liquid muriatic acid*, or *spirit of salt*. When pure it is perfectly colourless, but it generally has a yellow hue arising from accidental impurities. Its yellow colour is sometimes owing to muriate of iron: it is instantly destroyed by a few drops of muriate of tin, but this, instead of diminishing, obviously increases the impurity of the acid. When prepared by Woulfe's apparatus, the product in the second bottle is always perfectly pure. It sometimes contains sulphuric acid, which may be discovered by muriate of baryta occasioning a white precipitate, the acid may be purified by redistillation from a fresh portion of common salt.

Specific gravity of acid of commerce.

429. The specific gravity of the acid of commerce is generally about 1,166; but when obtained by means of Woulfe's apparatus, and especially when the bottles are surrounded by ice or snow, it approaches 1,500.† H.

Properties of the liquid acid.

430. Liquid muriatic acid emits white suffocating fumes, consisting of muriatic acid gas, which become visible by contact with the moisture of the air (373). When heated in a retort, the gas is disengaged, and may be collected over mercury. It is not decomposed by the contact of charcoal, or other combustible bodies. When diluted with water, an elevation of temperature is produced, less remarkable, however, than that occasioned by diluting sulphuric acid (42); and when the mixture has cooled to its former temperature, a diminution of volume is found to have ensued.

* In this table no notice is taken of the excess of water which is present, and which is employed in dissolving the muriatic acid, with which part of it distills over. Brande *Manual of Pharmacy*, 198.

† For the correspondence between its specific gravity and the quantity of real acid which it contains, see *Appendix*.

431. Muriatic acid combines readily with alkalis, and with most of the earths, both in their pure and carbonated state. Combines with alkalis.
H. 1. 272.

432. When liquid muriatic acid is brought into contact with any substance containing oxygen in a state of loose combination, the hydrogen of the acid unites with the oxygen and forms water, while the chlorine is liberated in a gaseous state. Decomposed by substances containing oxygen.
(312). It is in this way that chlorine is procured for the purposes of chemistry and the arts, but instead of liquid muriatic acid it is usual to substitute materials capable of furnishing the acid gas as already described.

433. Concerning the *nature of chlorine and muriatic acid*, the opinions of chemists have undergone frequent changes. By Scheele, the discoverer of chlorine, muriatic acid was conceived to be compounded of a certain base and an imaginary principle called *phlogiston*, of which it could be deprived by the action of certain bodies. But as it was afterwards found that all bodies which are capable of producing this change in muriatic acid contain oxygen, and that their proportion of oxygen is diminished by the process, it was concluded that what takes place in the action of metallic oxides on muriatic acid is simply the transfer of oxygen from the oxide to the acid, and the gas which resulted was then called *oxymuriatic*, or *oxygenated muriatic acid*. Nature of chlorine and muriatic acid.
This view of the subject was modified in consequence of the experiments of Sir H. Davy, and he was led to consider the *muriatic acid* as a compound of a certain basis with water, and the *oxymuriatic* as a compound of the same basis with oxygen. Scheele's Theory.
It was found, for example, that when a metallic oxide was heated in muriatic acid gas, oxymuriatic acid was obtained, and water appeared in a separate state. It was therefore evident that the acid gas must either have contained water ready formed; or the elements of water; or hydrogen capable of forming water with the oxygen of the oxide. Davy's.

434. Subsequent experiments led to a different theory, and oxymuriatic acid is now considered by Sir H. Davy, as a simple or undecomposed substance and muriatic acid as a compound of that simple substance with hydrogen. Thus, according to this view, to convert muriatic acid into chlorine we have only to abstract the hydrogen of the acid; and to convert chlorine into muriatic acid, we have only to supply it with hydrogen (366).

435. The oxymuriatic acid or *chlorine* (as it is now called) is supposed to unite at once with the metals, without requiring, like the sulphuric, nitric and other acids, that the metals should first be in the state of oxides.* H. 1. 275.

* For a full account of the opinions which have been maintained in regard to this subject, the reader is referred to the controversy between Drs Murray and J. Davy, in the 34th vol. of Nicholson's Jour.; to Sir H. Davy's paper in the Phil. Trans. for 1818, p. 169; to the 8th vol. of Trans. of the Royal Soc. Edin.; the Annals of Philosophy, xii. 379 and xiii. 26, 285; and to a paper by Mr R. Phillips, in the new series of that work, vol. i. p. 27, on the action of chlorides on water.

Hydro-bromic acid.

How obtained.

Action of heat, chlorine, potassium and tin.

Solution.

Action of chlorine and nitric acid.

Action of metallic oxides.

Analysis.

436. *Hydrogen and Bromine*.—No chemical action takes place between the vapour of bromine and hydrogen gas at common temperatures; but their combination is effected by the action of bromine on some of the gaseous compounds of hydrogen. Thus on mixing the vapor of bromine with hydriodic acid, sulphuretted hydrogen, or phosphuretted hydrogen gases, decomposition follows, and a colourless gas, possessed of acid properties is generated. To this gas the name of *Hydrobromic acid* is applied. A mixture of bromine and phosphorus, slightly moistened, yields a large quantity of pure hydro-bromic acid gas, which may be collected over mercury.

437. Hydro-bromic acid gas is colourless, has an acid taste and a pungent odour. It irritates the glottis powerfully, excites cough, and when mixed with moist air, yields white vapours, which are denser than those occasioned by muriatic acid.

438. It is not decomposed when transmitted through a red hot tube, either alone or mixed with oxygen. Chlorine decomposes it with the production of muriatic acid gas, and deposition of bromine. Potassium and tin decompose it with facility, the first at common temperatures, the last by the aid of heat.

439. Hydro-bromic acid is very soluble in water. The solution may be made by treating bromine with sulphuretted hydrogen dissolved in water, or still better, by transmitting a current of hydro-bromic acid gas through pure water. The liquid becomes hot during the condensation, acquires great density, increases in volume, and emits white fumes when exposed to the air. This acid solution is colourless when pure, but possesses the property of dissolving a large quantity of bromine, and then receives the tint of that substance.

440. Chlorine decomposes the solution of hydro-bromic acid in an instant. Nitric acid likewise acts upon it, though less suddenly, occasioning the disengagement of bromine, and probably the formation of water and nitrous acid. The *nitro-hydrobromic acid* is analogous to *aqua regia* and possesses the property of dissolving gold.

441. The metallic oxides, do not act in an uniform manner on the hydro-bromic acid. The alkalies, earths, the oxides of iron, and the peroxides of copper and mercury, form compounds which may be regarded as hydro-bromates; whereas the oxide of silver and the protoxide of lead, give rise to double decomposition, in consequence of which water and a metallic bromuret result.

442. When hydro-bromic acid is decomposed by potassium, a quantity of hydrogen remains precisely equal to half the volume of the gas employed; and when hydriodic acid gas is decomposed by bromine, the resulting hydro-bromic acid occupies the same space as the gas which is decomposed. It is hence apparent that 100 measures of hydro-bromic acid gas contain 50 measures of the vapour of bromine and fifty of hydrogen. T.

443. *Hydrogen and Iodine.*—When a mixture of hydrogen and the vapour of iodine is transmitted through a red hot porcelain tube, direct combination takes place and *hydriodic acid* gas is formed.

444. This gas may be obtained by the action of water on the iodide of phosphorus. Any convenient quantity of moistened iodine is put into a small glass retort, and about one twelfth of its weight of phosphorus is then added. An iodide of phosphorus is formed, which reacts upon the water. Mutual decomposition ensues; the oxygen of the water unites with the phosphorus, and the hydrogen with the iodine, giving rise to the formation of phosphoric and hydriodic acids. On the application of a moderate heat, the latter passes over in the form of a colourless gas.

How obtained:

445. Hydriodic acid is very sour, and smells like muriatic acid. Its specific gravity was found, by experiment to be 4,443, by calculation, to be 4,428; compared with hydrogen its specific gravity is 62,5 to 1; 100 cubic inches weighing 133,6 grs. H. 1. 279.*

Properties.

446. It is decomposed by Voltaic electricity, iodine appearing at the positive, and hydrogen at the negative pole.

Effect of electricity,

447. It is instantly decomposed by chlorine, which produces muriatic acid and the blue vapour of iodine is rendered evident. These gases often take fire on mixture.

of chlorine,

It is decomposed by those oxides which hold their oxygen loosely, and combines with the rest, forming neutral salts called *hydriodates*.† H. 1 281.

of oxides.

448. That Hydriodic acid gas consists of equal volumes of hydrogen and vapour of iodine is shown by the action of mercury, which by absorbing the iodine, evolves half a volume of hydrogen from one of the gas.

Composition.

449. It is composed by weight, according to Gay-Lussac, of 100 iodine and 0,849 hydrogen; but correcting the specific gravity of hydrogen gas to 0,0694 its true composition will be, by weight

| | | | |
|----------|----------|-----------|-----|
| Hydrogen | . 1 atom | | 1 |
| Iodine | . 1 “ | | 125 |

Weight of its atom 126. H.

Oxygen being = 1 the atomic weight would be 15,625. T.

450. Hydriodic acid gas is rapidly absorbed by water, the solution is fuming and has the density of 1,7. The solution exposed to a temperature below 260° becomes concentrated by loss of water; at about 260° it boils, and may be distilled. It becomes dark coloured when kept, in consequence of a partial decomposition, and it readily dissolves iodine, becoming of a deep brown colour.

* Dr Thomson makes the specific gravity 4,34027 air = 1, and the weight of 100 cubic inches 132,3785.
† Of these salts, that with base of potassa is used in medicine; a process for preparing it advantageously is described in the *Ann. of Philos*, N. S. vii. 468.

Liquid acid,
how best
prepared.

451. The liquid hydriodic acid is best prepared by passing sulphuretted hydrogen through a mixture of iodine and water; the hydrogen unites with the iodine, and the sulphur is precipitated, and on heating and filtering the liquor, a pure solution of hydriodic acid is obtained, which may be concentrated by evaporation. Till it attains the temperature of 257° water only distils; above this point, the acid itself is volatilized and remains stationary at $262\frac{1}{2}^{\circ}$, its density being then 1.7. With solutions of lead it gives a fine orange precipitate, with solution of peroxide of mercury, a red one; and with silver a white precipitate, insoluble in ammonia.

SECTION II. Nitrogen.

Discovery.

452. This was first recognised as a distinct æriform fluid by Dr Rutherford, in 1772. (Thesis, *De Aere Mephitico*.) It may be obtained by heating phosphorus in a confined portion of dry atmospheric air, which consists of nitrogen and oxygen; the phosphorus absorbs the latter, and the former gas remains. After repeated washing it may be considered as pure.

How ob-
tained.

453. It may also be obtained by inverting a jar full of common air over a mixture of equal weights of iron filings and sulphur made into a paste with water. But this process requires much time.

Other pro-
cesses.

A quicker process, for procuring nitrogen gas, consists in filling a bottle, about one 4th, with a solution of nitrous gas in liquid sulphate of iron, or with liquid sulphuret of lime, and agitating it with the air, which fills the rest of the bottle. During the agitation, the thumb must be firmly placed over the mouth of the bottle; and, when removed, the mouth of the bottle must be immersed in a cup full of the same solution, which will supply the place of the absorbed air. The agitation, and admission of fluid must be renewed, alternately, as long as any absorption takes place.

Nitrogen may be procured from the lean part of flesh meat, (beef for example), which may be put into a gas bottle, along with very dilute nitric acid. By a heat of about 100° , the gas is disengaged, and may be collected over water. Its source has been satisfactorily traced to the animal substance, no part of it proceeding from the nitric acid.

Derivation of
azote.

454. This gas is fatal to animal life and was, on this account, named by Lavoisier *Azote* or *Azotic gas*, derived from the Greek privative α and $\zeta\omega\eta$, life. This being but a negative property, has been deemed an improper foundation for its nomenclature; and the term nitrogen has been substituted, because one of the most important properties of its base is, that by union with oxygen, it composes nitric acid. H. 1. 281.

455. Nitrogen is not inflammable; and a lighted taper immersed in it is extinguished. Even phosphorus in a state of active inflammation is instantly extinguished by it. This is best shown by placing the burning phosphorus in a tin cup raised by a stand, fig. 36, over the surface of the water, and quickly inverting over it a jar filled with nitrogen gas. Exp.
Pl. 2.

456. When mixed with pure oxygen gas, in the proportion of four parts to one of the latter, it composes a mixture resembling atmospheric air in all its properties. Of this any one may be satisfied, by mixing four parts of nitrogen with one of oxygen gas, and immersing in the mixture, a lighted taper. The taper will burn as in atmospherical air. H. Exp.

457. It is not absorbed by water. It is a little lighter than atmospheric air, 100 cubic inches being found by Sir H. Davy to weigh 30,04 grains under a pressure of 30 inches, and at the temperature of 55° Fahrenheit. At 60° Fahrenheit, 100 inches weigh, therefore, 29,73 grains. According to Dr Thomson its specific gravity is 0,9722 air = 1; 0,875 oxygen = 1; and 100 cubic inches weigh 29,6527 grains.

458. That nitrogen is not an element, but itself a compound, has been long suspected, and various attempts have been made to discover its ingredients. Berzelius, from the combination of experiment with much theoretical reasoning, has deduced, that nitrogen is compounded of oxygen and an unknown base.* This base, however, is purely hypothetical; and has never yet been exhibited in a separate state. Berzelius has proposed for it the name of *nitricum*. Composition
of nitrogen.

459. When the compounds of nitrogen are submitted to Voltaic decompositions, it is attracted by the negative pole.

460. *Nitrogen and oxygen.*—When nitrogen and oxygen gases are mingled together, in whatsoever proportions they are employed, no combination ensues. The result is a simple mixture of the two gases, which do not, like inelastic fluids, separate on standing, but remain diffused through each other for an indefinite length of time. When, however, either one or both of these elements is in a condensed state, or deprived of part of that caloric which keeps the gravitating particles of all gases at a distance from each other, they unite and form compounds, distinguished by very striking properties. According to the proportions in which the oxygen and nitrogen exist in these compounds, their qualities undergo a remarkable variation; so that from two elementary bodies, variously united, we have several compounds, totally unlike each other in external qualities, as well as in their chemical relations. General view
of the com-
pounds of
nitrogen and
oxygen.

461. In a series of the compounds of nitrogen, founded on their proportion of oxygen, they occupy (excluding atmospherical air from the number) the following order, the last containing the largest proportion of oxygen; nitrous oxide—nitric oxide or nitrous gas—hypo-nitrous acid—nitrous acid or nitrous vapour

* 2 Ann. Philos. 284.

--and nitric acid. The two first are sparingly soluble in water; but the three last unite with it largely, and form liquid compounds of decidedly acid taste and quality. H. 1. 297.

Nitrous oxide.

462. *Protoxide of Nitrogen*, or *nitrous oxide*, may be obtained by several processes. By dissolving zinc, or tin, in nitric acid, diluted with five or six times its weight of water. Zinc, during this solution disengages nitrous oxide till the acid begins to exhibit a brownish colour, when the process must be suspended, as nitrous gas is then formed. But the gas thus obtained is impure.

Process for obtaining.

463. To procure it in a state of purity, a salt, to be hereafter described, called *nitrate of ammonia*, is heated in a retort over an Argand lamp. The heat should not be raised beyond 440° F. The salt will presently liquefy, and must be kept gently simmering, avoiding violent ebullition. The gas may be collected over water, and allowed to stand for a few hours before it is used, during which time it will deposit a white substance, and become perfectly transparent.

A gazometer best adapted for its reception.

464. A gazometer, however, is best adapted for its reception, because all danger is then avoided of the water of the trough being forced into the retort; and because the gas is brought into contact with a much smaller surface of water, which has the property of absorbing a considerable proportion of the gas. On this account, water which has been once used to confine the gas, may be kept for the same purpose.

Theory of this process.

465. The changes that take place during the conversion of nitrate of ammonia into nitrous oxide, are the following. Nitric acid is composed of oxygen and nitrous gas, ammonia of hydrogen and nitrogen. In a high temperature, the nitrous gas combines with an additional dose of nitrogen, and forms nitrous oxide; while the oxygen of the decomposed nitric acid unites with the hydrogen of the ammonia, and forms water.

Synonyms, &c.

466. The gas thus obtained, was termed, by its discoverer, Dr Priestley, *dephlogisticated nitrous air*; by the Dutch chemists *gaseous oxide of azote*. Its most appropriate title is *protoxide of nitrogen*.*

Specific gravity.

467. It is considerably heavier than common air. Sir H. Davy has stated 100 cubic inches (at 30 inches pressure and at 60° F.) to weigh between 48 and 49 grains; and hence its specific gravity should be very nearly 1.6. According to Dr Thomson, 100 cubic inches weigh 46,5972 grs. and its specific gravity, air = 1, is 1,5277; oxygen = 1, 1,375.

Liquefaction of nitrous oxide.

468. Mr Faraday has obtained nitrous oxide in a liquid form, under a pressure of above 50 atmospheres. For this purpose nitrate of ammonia previously made as dry as could be, was sealed up in a bent tube, and then heated in one end, the other being kept cool. Two fluids were thus obtained; the heavier, proved to be water with a little acid and nitrous oxide in solution; the other was nitrous oxide in a liquid state. It was

* For a full account of this gas, see Sir H. Davy's *Researches*, Lond. 1800.

colourless, limpid, and so volatile, that the warmth of the hand caused it to disappear in vapour. It boiled readily by the difference of temperature between 0 and 50°. It had no tendency to solidity at—10°. A tube being opened in the air, the nitrous oxide instantly burst into vapour, and another tube being opened under water, the gas was collected.*

469. Sir H. Davy discovered that nitrous oxide may be taken into the lungs with safety,† and that it supports respiration for a few minutes. A few deep inspirations of it are followed by most agreeable feelings of excitement, similar to the early stages of intoxication. May be re-
spired.

The experiment of breathing this gas, however, cannot be made with impunity, especially by those who are liable to a determination of blood to the head.‡

470. Nitrous oxide has a distinctly sweet taste, and a peculiar but agreeable odour. Water takes up about its own bulk of this gas, and evolves it again unchanged when heated.

471. Nitrous oxide supports combustion, and a taper introduced into it has its flame much augmented and surrounded by a purplish halo. Phosphorus and sulphur, when introduced in a state of vivid ignition into this gas, are capable of decomposing it, and burn with the same appearance nearly as in oxygen; but, if when put into the gas, they are merely burning dimly, they then do not decompose it and are extinguished, so that they may be melted in the gas, or even touched with a red hot wire without inflaming, (but when wire intensely heated, or made white hot, is applied, the phosphorus burns, or rather detonates, with prodigious violence. H.) Charcoal, and many of the metals, also decompose nitrous oxide at high temperatures. Supports
combustion.

472. A mixture of this gas with hydrogen gas detonates, on applying a lighted taper, or passing an electric spark, and is decomposed also by spongy platinum at common temperatures. Nitrous oxide forms a combustible mixture with ammoniacal gas,|| 100 measures of the latter requiring for perfect decomposition 150 of nitrous oxide. It burns also when mixed with olefiant gas§ and Dr Henry has pointed out an easy and summary way of analyzing it, by firing it over mercury with carbonic oxide.¶ In this case 1 vol. of nitrous oxide is decomposed by Detonates
with hydro-
gen.

* *Phil. Trans.* 1823, p. 195.

† *Researches on the nitrous oxide.*

‡ In order to ascertain whether nitrous oxide be adulterated with either common air or oxygen gas we may mix equal measures of the gas under examination, and of nitrous gas. If any diminution ensue, the presence of one of these may be suspected; and the amount of the diminution will show which of them is contained in it. Nitrous gas, however, is a much more common contamination; for it is generated, along with nitrous oxide whenever the temperature of the salt is raised too high. Its presence may be detected, either by red fumes and a diminution on the admixture of oxygen gas; or by an absorption being effected, on agitating the gas with a solution of green sulphate of iron, which has no action on pure nitrous oxide. H. 1. 302.

|| Henry in *Philos. Trans.* 1809, p. 444.

§ Davy, *Researches*, p. 373.

¶ *Ann. of Philos.* N. S. viii. 299.

1 vol. of carbonic oxide, and there result 1 vol. of carbonic acid and 1 vol. of nitrogen. On this is founded a ready and correct method of testing the purity of nitrous oxide.*

Decomposition.

Pl. 4.

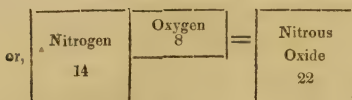
473. At a red heat this gas is decomposed and converted into nitrogen and nitric oxide, undergoing at the same time an increase of bulk. For experiments of this kind the following simple apparatus may be used: It consists of two bladders, fig. 99, one of which is filled with the gas, and the other empty, attached to the extremities of a porcelain tube which traverses the body of a furnace. The bladders are supplied with stop-cocks, and the gas is squeezed from one to the other when the tube is red hot.

Analysis of nitrous oxide.

474. The best analysis of this gas is effected by detonation with hydrogen; one volume of nitrous oxide requires one volume of hydrogen. This mixture fired by the electric spark, produces water, and one volume of nitrogen remains. Now, as one volume of hydrogen takes half a volume of oxygen to form water, nitrous oxide must consist of two volumes of nitrogen and one volume of oxygen; these three volumes being so condensed in consequence of chemical union, as only to fill the space of two volumes. The specific gravity of nitrogen compared with oxygen, is as 14 to 16; nitrous oxide, therefore, consists of

14 Nitrogen
8 Oxygen

Number for nitrous oxide, = 22†



Nitrous gas.

475. *Nitric oxide, deutoxide of nitrogen, or nitrous gas.*—This gas, though discovered by Dr Hales, was first examined by Dr Priestley, and called by him *nitrous* air, a term afterwards changed to *nitrous gas*, then to *nitric oxide*, and more lately to *deutoxide of azote*, or *deutoxide of nitrogen*, which last appears to be its most appropriate title. It is more generally known, however, under the name of nitrous gas. H.

How obtained.

Pl. 3.

476. It is usually obtained by presenting certain substances to nitric acid, which abstract a portion of its oxygen, leaving the remaining elements in such proportions as to constitute the gas in question; for this purpose some copper filings may be put into a gas bottle, (fig. 65,) with nitric acid, diluted with thrice its bulk of water; an action ensues, red fumes are produced, and there is a copious evolution of the gas, which may be collected and preserved over water. The first portions should be rejected as containing nitrogen and nitrous acid gas. Nitric

* See Henry's *Chemistry*, vol. 1. p. 309, edit. 10th.

† Taking oxygen as = 1 the atomic weight of nitrous oxide is 27.5. T.

oxide is presently recognized by the red fumes which it produces when brought into the contact of air. During this process part of the nitric acid gives oxygen to the copper; and passes to the state of nitrous gas, and the remaining acid unites with the deutoxide of copper, and composes the deutonitrate of that metal. Theory of the process.

477. Quicksilver may be substituted for the copper; but in the latter case it will be found necessary to apply heat to the materials. H. 1. 306.

478. When mixed with oxygen gas red fumes arise, heat is evolved, a diminution takes place, and if the two gases be in proper proportion, and perfectly pure, they disappear entirely. The product of this union is possessed of acid properties, which may be shown by the following experiment. Effect of oxygen.

Paste a slip of litmus-paper within a glass jar, near the bottom; and into the jar, filled with and inverted in water, admit as much nitrous gas, previously well washed, as will displace the water below the level of the paper. The colour of the litmus will remain unchanged; but on adding oxygen gas it will be immediately reddened. H. 311. Exp.

479. Nitrous gas is rather heavier than common air; 100 cubic inches at 60° F. barometer 30, weigh 32 grains, and its specific gravity is 1,050.* According to Dr Thomson 100 cubic inches weigh 31,7708 grains and its specific gravity is 1,04166, air = 1, or 0,9375 oxygen = 1. Its specific gravity to hydrogen is as 15 to 1. Specific gravity.

480. When it has been washed with water it is not acid, as proved by the colour of the litmus remaining unchanged by it. (472.) Properties.

481. It extinguishes most burning bodies; but phosphorus readily burns in it if introduced in intense ignition. Mingled with hydrogen gas it imparts a green colour to its flame. A mixture of hydrogen and nitrous gas is decomposed by spongy platinum at common temperatures.

482. Nitrous gas is decomposed by exposure to almost all bodies that attract oxygen. Thus iron filings decompose it, and become oxidized, affording a proof of the presence of oxygen in this gas. During this process, water, ammonia, and nitrous oxide, in the proportion of one volume from two of nitrous gas, are generated. Sulphuret of potassa, &c. have a similar effect. Sulphuret of baryta gives one half its volume of nitrogen. Mixed with sulphurous acid, nitrous gas is decomposed, and this acid is changed into the sulphuric, but not unless water is present.† Nitrous gas, does not, with hydrogen gas, afford a mixture that can be exploded by the electric spark, but, with ammoniacal gas, it may be fired in a Volta's eudiometer over mercury. The oxygen of the nitrous gas unites with the hydrogen of the ammonia, and the nitrogen of both gases is set at liberty. H. 1. 311. Decomposition.

* Davy.

† Nicholson's Jour. xvii. 43.

483. Bodies that have a still more powerful affinity for oxygen, resolve nitrous gas into its *ultimate* elements, arsenic, zinc or potassium, when heated in it, evolve half its volume of nitrogen.

If therefore we call nitrous oxide a compound of 1 proportional, or atom, of nitrogen + 1 of oxygen, then nitrous gas may be considered as consisting of 1 nitrogen + 2 oxygen, or by weight, 14 nitrogen + 16 oxygen, and its symbol will stand thus

| | | | |
|----------|--------|---|-------------|
| Nitrogen | Oxygen | = | Nitrous gas |
| 14 | 8 | | |
| | 8 | | 30 |

Exp,

A piece of glowing charcoal plunged into nitrous gas is presently extinguished, but if it be passed through a porcelain tube containing red hot charcoal, nitrogen and carbonic acid and oxide are produced. B.

Analysis.

484. Its composition was ascertained by Sir H. Davy by the combustion of charcoal. Two volumes of the gas yielded one volume of nitrogen and about one of carbonic acid; * whence it was inferred to consist of equal measures of oxygen and nitrogen united without any condensation. Gay-Lussac and Dr Henry have proved the same fact. When potassium was heated in 100 measures of the gas, 50 measures of pure nitrogen were left, and the loss of weight corresponded to 50 measures of oxygen.†

485. Nitrous gas is absorbed by the green sulphate and muriate of iron, which do not absorb nitrogen gas. To ascertain therefore how much nitrogen gas a given quantity of nitrous gas contains, it may be agitated in a tube with one of these solutions. This solution is employed in eudiometry.

Nitrous gas
and chlorine.

486. *Nitrous Gas and Chlorine*, when both are perfectly dry, exert no mutual action, but the presence of water causes an immediate change; it is decomposed, and, furnishing oxygen to the nitric oxide, and hydrogen to the chlorine, nitrous acid and muriatic acid gases are generated. It was the presence of water which misled those, who thought that the red fumes produced by mixing nitric oxide and chlorine not carefully dried, resulted from the existence of oxygen in chlorine.

487. *Hypo-nitrous Acid*.—Gay-Lussac has concluded from his experiments that there exists a compound of nitrogen and oxygen intermediate between nitric oxide and nitrous acid, which he has termed *per-nitrous acid*, but to which the term *hypo-nitrous acid* is more applicable. He considers it a compound of 1 proportional of nitrogen, and 3 of oxygen.

Its existence
hypothetical.

When 400 measures of nitrous gas, and 100 measures of oxygen (in which, taken together, the nitrogen and oxygen are to each other by measure as 100 to 150) are mixed together

* Davy's *Elements*, p. 200. † *Memoires d' Arcueil*.

over a solution of potassa confined by mercury, we obtain 100 measures of this compound,* which however, is so far hypothetical that it has never yet been exhibited in a separate form, for when a stronger acid is added, to expel it from the potassa, it is resolved into nitrous gas and nitrous acid.

Absorbed by solutions of iron.

488. Hypo-nitrous acid contains three times more oxygen than the protoxide of nitrogen; so that by weight, it is formed of

Composition.

| | | | |
|----------|----|---|----------|
| Nitrogen | 14 | - | 1 atom. |
| Oxygen | 24 | - | 3 atoms. |

Weight of its atom 38

489. *Nitrous Acid Gas*.—When nitric oxide is presented to oxygen, the two gases combine, and a new gaseous compound of a deep orange colour results.

Nitrous acid gas.

Into a large glass globe, or other convenient vessel, previously filled with water, introduce sufficient nitrous gas to displace about two thirds of the water. On passing into it oxygen gas the vessel will become filled with deep orange coloured nitrous acid gas.

Exp,

This compound is not easily examined, because it is absorbed both by quicksilver and water, so that to preserve it for examination, we are obliged to resort to exhausted glass vessels. When we thus mix two volumes of nitric oxide with one volume of oxygen, the gases become condensed to about half their original volume, and form *nitrous acid gas*.

Not easily examined.

490. This gas supports the combustion of the taper, of phosphorus, and of charcoal, but extinguishes sulphur. It is readily absorbed by water, forming a greenish liquid.†

Properties:

It is obvious that this nitrous acid gas must consist of 14 nitrogen + 32 oxygen, and therefore, its number is 46; for nitric oxide is composed of equal volumes of nitrogen and oxygen, and one additional volume of oxygen, or two proportionals by weight, are added to form nitrous acid.

Composition.

| | | | |
|----------|--------|------|-----------------------|
| Nitrogen | Oxygen | } 32 | Nitrous Acid 46 |
| 14 | 8 | | |
| | 8 | | |
| | 8 | | |

491. If the mixture of nitric oxide and oxygen be made over water, in the above proportions, and if the gases be perfectly pure, complete absorption takes place; but if either the oxygen or nitric oxide contain uncombined nitrogen it will remain unabsorbed.

Absorbed by water.

492. Nitrous acid may exist in the liquid as well as in the gaseous form. To form liquid nitrous acid, nothing more is necessary than to saturate water with this vapour. The water becomes first green, then blue, and finally an orange colour,

Liquid nitrous acid.

* *Ann. de Chimie et Phys.* I. 400.

† It reddens litmus paper, has a sour taste, a strong smell and turns animal substances yellow.

more or less deep. The latter may be brought to the state of green or blue by adding more or less water. Hence the colour depends partly on the circumstance of density; but there can be little doubt that it is materially affected also by the proportions of nitric, nitrous, and hypo-nitrous acids, which according to Gay-Lussac, compose nitrous acid, as it is ordinarily obtained in a liquid state. H. 1. 321.

From nitrate
of lead.

493. It may be procured by exposing nitrate of lead, carefully dried to a heat sufficient to decompose the salt. The nitric acid of the salt is resolved into nitrous acid and oxygen; and if the products are received in vessels kept moderately cool, the greater part of the former condenses into a liquid. This substance was first obtained by Gay-Lussac, who regarded it as hypo-nitrous acid; but M. Dulong has proved by a careful analysis that it is anhydrous nitrous acid.

Properties.

The liquid anhydrous acid is powerfully corrosive, has a strong acid taste and pungent odour, and is of a yellowish orange colour. Its density is 1,451. It remains liquid at ordinary temperatures and pressure, and boils at 82° F. Exposed to the air it evaporates with great rapidity, forming the common nitrous acid vapours, which, when once mixed with air or other gases, require an intense cold to condense them.

The action of water on anhydrous nitrous acid is very remarkable. T.

Nitric Acid.

494. *Nitric Acid.*—If a succession of electric sparks be passed through a mixture of oxygen and nitrogen gases confined in a glass tube over mercury, a little water being present, the volume of the gases will gradually diminish, and the water after a time will be found to have acquired acid properties. On neutralizing the solution with potassa, or what is better, by putting a solution of pure potassa, instead of water, into the tube, a salt is obtained which possesses all the properties of the nitrate of potassa (nitre.) This experiment was performed by Mr Cavendish in 1785, who inferred from it that nitric acid is composed of oxygen and nitrogen.

How formed.

495. The nitric acid may be formed more conveniently by adding nitrous gas slowly over water to an excess of oxygen gas. Gay-Lussac proved that the nitric acid might in this manner be obtained quite free from the nitrous or hypo-nitrous acids; and that it is composed of 100 measures of nitrogen, and 250 of oxygen. This result agrees with the proportions deduced by Sir H. Davy, and is confirmed by an analysis of the nitrate of baryta recently made by Dr Henry. T.

Composition.

496. Nitric acid is therefore composed of 1 proportional of nitrogen = 14, & 5 of oxygen = 40, and this will be the symbol representing its composition,

| | | |
|-----------|--------|------|
| Nitrogen. | Oxygen | } 40 |
| 14 | 8 | |
| | 8 | |
| | 8 | |
| | 8 | |

Consequently, the representative number of *dry* nitric acid is 54,0. But in its liquid state it always contains water; and when in this state its specific gravity is 1,5, it may be regarded as a compound of one proportional of dry acid and two of water, which may be numerically expressed thus:

Acid. Water.

$$54 + 18 = 72, \text{ liquid acid.}$$

497. Nitric acid cannot exist in an insulated state. The most simple form under which chemists have hitherto procured nitric acid is in solution with water. It is usually obtained by the distillation of purified nitre with sulphuric acid, of which materials different proportions are employed.

Into a glass retort, which may be either tubulated or not, put four parts by weight of nitrate of potassa, reduced to a coarse powder, and pour upon it three parts of concentrated sulphuric acid. Apply a tubulated receiver of large capacity, between which and the retort, an adopter may be interposed; these junctures being luted with a mixture of pipe-clay, sifted sand, and cut tow or flax. To the tubulare of the receiver, a glass tube may be fixed by means of the fat lute,* and may terminate in another receiver, containing a small quantity of water.

Process for
obtaining
nitric acid,

If the operator wishes to collect the gaseous products also, this second receiver should be provided with a tubulure, to which a bent pipe may be luted, terminating under one of the inverted funnels in the shelf of the pneumatic trough. Apply heat to the retort, through the intervention of the sand-bath. The first product, that passes into the receiver, is generally of a red colour, and of a smoking quality. These appearances gradually diminish; and if the materials used were clean, the acid will come over pale, and even colourless. Afterwards it gradually re-assumes a red colour, and smoking property; which appearances go on increasing till the end of the operation; and the whole product, mingled together, has either a yellow or an orange colour, according to the temperature employed. H. 1. 318.

498. The nitric acid of commerce, which is generally red and fuming in consequence of the presence of nitric oxide, is procured by the distillation of two parts of nitre with one of sulphuric acid; these proportions afford about one part of orange-coloured nitric acid of the specific gravity of 1,48. Upon the large scale 112 lbs. of nitre, and 56 of sulphuric acid yield from 50 to 52 lbs. of nitric acid. Some manufacturers employ three parts of nitre and two of sulphuric acid, and the *London Pharmacopœia* directs equal weights, by which a nearly colourless nitric acid is afforded.

on the large
scale.

* Formed by heating perfectly dry and finely sifted tobacco pipe clay, with painters' drying oil.

Proportions
of acid and
water.

It will appear by referring to the article *Sulphuric Acid*, that it contains in its liquid state one proportional of dry acid, and *one* of water; whereas liquid nitric acid contains one proportional of dry acid, and *two* of water; hence the requisite excess of sulphuric acid, where colourless and perfect nitric acid is to be obtained; hence too the red colour of the acid of commerce in consequence of the smaller quantity of sulphuric acid generally used by the manufacturer. This will be more apparent by reference to the article *Bi-sulphate of Potassa*.*

Purification
of nitric acid.

499. The nitric acid of commerce, as usually obtained is impure, and muriatic and sulphuric acids may often be detected in it. The former may be separated by *nitrate of silver*, or *nitrate of lead*, and the latter by a very dilute solution of *nitrate of baryta*. To obtain *pure nitric acid*, therefore, add to that of commerce a solution of nitrate of silver, as long as it produces any white precipitate; and when this has subsided, pour off the clear liquor, and add, in the same way, the nitrate of baryta; then distil the acid, and it will pass over perfectly pure.

Pl. 4.

The distillation of nitric acid may be conducted upon the small scale in a tubulated glass retort *a*, with a tubulated receiver *b*, passing into the bottle *c*, fig. 100. The requisite heat is obtained by the lamp *d*, and the whole apparatus supported by the brass stands with sliding rings *e e*.†

For pharmaceutical purposes, the ordinary acid is generally sufficiently pure. If, however, pure nitre, and pure sulphuric acid be employed in its production, and the latter not in excess, there is little apprehension of impurity in the resulting acid.

Specific grav-
ity.

500. Liquid nitric acid is heavier than water, in the proportion of 1,5 or upwards to 1. Proust obtained it as high as 1,62; and the specific gravity of real nitric acid, which cannot, however, be obtained separately, may be calculated at 1,75. In its heaviest form, it still contains a portion of water, which is essential to its existence in a liquid state, and without which its elements would separate from each other. In acid of the sp. gr. 1,50 the water amounts, calculating from the data furnished by Dr Wollaston, to 25,11 grains in 100 grains of acid; or, according to Mr R. Phillips, to 25,09. According to Sir H. Davy, the strongest acid (sp. gr. 1,55) contains 14,4 parts of

* If it be required to decompose the whole of any portion of nitre, it is necessary to use as much sulphuric acid, as will form, with the alkali of the nitre, *bi-sulphate of potassa*, viz. 97 parts of acid, of density 1,85 to 100 parts of nitre. H. 1. 319.

Preparation
of nitrous
acid, or aqua-
fortis.

Pl. 5.

† The manufacturer who prepares nitric acid upon a large scale, generally employs distillatory vessels of stone ware. Fig. 101 represents the arrangement of the distillatory apparatus, employed at Apothecaries' Hall, London, for the production of common *aqua fortis*: it consists of an iron pot, set in brick-work, over a fire-place; an earthenware head is luted upon it, communicating with two receivers of the same material, furnished with earthenware stop-cocks, the last of which has a tube of safety dipping into a basin of water.

water in 100; and acid of sp. gr. 1,42 contains 25,2 of water in 100.*

501. Nitric acid is usually coloured by nitrous acid gas, to expel which, put the acid into a retort to which a receiver is applied, the two vessels not being luted, but joined merely by paper. Apply a very gentle heat for several hours to the retort, changing the receiver as soon as it becomes filled with red vapours. The nitrous gas will thus be expelled, and the nitric acid will remain in the retort limpid and colourless. It must be kept in a bottle secluded from light.† H. 327.

Coloured by
nitrous acid
gas.

502. Nitric acid emits white fumes when exposed to the air, and is extremely sour and corrosive.

It gives a yellow stain to the skin.

It boils at 248° Fahrenheit, and may be distilled over without any essential change. This, however, is true only of acid of the specific gravity 1,4237; for an acid, weaker than this, is strengthened by being boiled; while an acid, stronger than 1,4237, becomes weaker by boiling. All the varieties of nitric acid, therefore, are brought, by sufficient boiling, to the specific gravity 1,4237, which appears to be the most energetic combination of acid and water.

Boiling point.

503. Nitric acid may be frozen by the application of a sufficiently low temperature. Like sulphuric acid, there is a certain point of density at which it most readily congeals. Mr Cavendish has described this, not by its specific gravity, but by the quantity of marble which it is capable of dissolving. When it takes up $\frac{4,16}{1000}$ ths of its weight, in which case its specific gravity is 1,3, the acid freezes at 2° below 0 Fahrenheit. When considerably stronger and capable of dissolving $\frac{5,61}{1000}$ ths, it required cooling to—41,6; and when so much diluted as to take up only $\frac{2,76}{1000}$ ths, it did not congeal till cooled to—40,3.‡

May be frozen.

504. Strong nitric acid absorbs moisture from the atmosphere; in consequence of which it increases in weight, and diminishes in specific gravity.

Absorbs moisture.

505. When two parts of the acid are suddenly diluted with one of water, an elevation of temperature is produced to about 120° F.; and the admixture of 58 parts by weight of acid of specific gravity 1,50 with 42 parts of water, both at 60° F., gives a temperature of 140°.§ When more water is added to

Mixed with water, temperature rises.

* Dr Thomson by using, in the decomposition of anhydrous nitre, only half its weight of concentrated sulphuric acid obtained nitric acid of sp. gr. 1,534. From an analysis of this he infers that acid of sp. gr. 1,55 is a compound of 1 atom of acid and 1 atom of water, or it contains

| | | | |
|-----------|--------------|-----------|----|
| Real acid | 85,714 parts | - - - - - | 54 |
| Water | 14,286 " | - - - - - | 9 |
| | 100. | | 63 |

When the full quantity of sulphuric acid was used he found the sp. gr. of the product only 1,4855 and that it is a compound of 1 atom real acid and 2 atoms of water.—For a table of the composition of nitric acid of different densities, see *Appendix*.

† An excellent test of the presence of even very small proportions of nitrous acid has been discovered by Gay-Lussac in the red sulphate of manganese, which is instantly deprived of colour by perfect nitric acid,

‡ *Phil. Trans.* 1788.

§ Dr Ure.

this diluted acid, its temperature is reduced. Snow or ice added to the cold dilute acid is instantly liquefied and an intense degree of cold is produced.

Effect of solar light. 506. When very concentrated it becomes coloured by exposure to the sun's light, passing first to a straw colour, and then to a deep orange. This effect is produced by the union of the light of the sun with oxygen, in consequence of which the proportion of that principle to the nitrogen is diminished.

Affords oxygen. 507. By exposing it to the sun's rays in a gas bottle, the bent tube of which terminates under water, oxygen gas may be procured. H. 1. 321.

Decomposed by combustibles, 508. This acid retains its oxygen with but little force,—hence it is decomposed by all combustible bodies, which are oxygenized by it, with more or less rapidity in proportion to their affinity for oxygen.

Exp. Poured on perfectly dry and powdered charcoal it excites the combustion of the charcoal, which becomes red hot, and emits an immense quantity of fumes.

It also inflames essential oils when suddenly poured on them.

Exp. Into a gallipot, placed upon a hearth and containing about a table-spoonful of oil of turpentine, pour about half the quantity of strong nitrous acid, previously mixed with a few drops of sulphuric acid. The moment the acids come in contact with the turpentine a large quantity of dense smoke will be produced, often accompanied with flame. The acid should be poured from a bottle tied to the end of a long stick, otherwise the operator's eyes may be severely injured.

Caution. 509. It is also decomposed by metals, as iron, tin, zinc, copper, &c. and with different phenomena, according to the affinity of each metal for oxygen.

Exp. This may be seen by pouring some strong nitric acid on iron filings, or powdered tin. The acid must be of greater density than 1.48, otherwise it will not produce the effect. Violent heat, attended with red fumes, will be produced, and the metals will be oxidized. H. 1. 323.

And by a red heat. 510. Nitric acid may be decomposed by passing its vapour through a red hot porcelain tube; oxygen is given off, nitrous acid gas is produced, and a quantity of diluted acid passes over into the receiver, having escaped decomposition; so that it is thus proved to consist of nitrous acid gas, oxygen and water.

For experiments of this kind the form of apparatus, described for the decomposition of water by iron (391), may be employed, omitting the condensing worm-pipe.

Synthesis. The nature of nitric acid was first synthetically demonstrated by Mr Cavendish, who passed electric sparks through a portion of atmospheric air, or through a mixture of one part of nitrogen and two of oxygen, confined over mercury. After some time the mixture diminished in bulk, and, on admitting a little water, an acid solution was obtained, which afforded crystals of nitre when saturated with potassa.

Uses. 511. Nitric acid is of considerable use in the arts. It is employed for etching on copper, as a solvent of tin to form with

that metal a mordant for some of the finest dyes; in metallurgy and assaying; in various chemical processes, on account of the facility with which it parts with oxygen and dissolves metals; in medicine as a tonic, &c. For the purposes of the arts it is commonly used in a diluted state, and contaminated with the sulphuric and muriatic acids, by the name of *aqua-fortis*. This is often prepared by mixing common nitre with an equal weight of sulphate of iron, and half its weight of the same sulphate calcined, and distilling the mixture; or by mixing nitre with twice its weight of dry powdered clay, and distilling in a reverberatory furnace. Two kinds are found in the shops, one called *double aquafortis*, which is about half the strength of nitric acid; the other simply *aquafortis*, which is half the strength of the double. U. 72.

Aqua-fortis.

512. Dr Liebig proposes the following process for detecting the presence of nitric acid. The fluid to be examined is to be mixed with as much sulphate of indigo as will give it a distinct blue colour, and after adding a few drops of sulphuric acid the mixture is to be boiled. If the fluid contains a nitrate, the blue colour will be discharged, or only rendered yellow if the quantity of nitrate is very minute. Dr Leibig states that by this process nitric acid may be detected when there is not more than a 400th of it present; by adding a little common salt to the fluid before applying the heat, even a 500th of nitric acid may be readily detected.* Gold leaf is a delicate test of the presence of uncombined nitric acid, a liquid which contains no chloric acid, and which is unable to dissolve gold leaf, but acquires the property of doing so when pure muriatic acid is added to it, must contain nitric acid. T.

Test of nitric acid.

513. *Nitro-muriatic Acid*.—This term has been applied to the *Aqua Regia* of the alchemists. When nitric and muriatic acids are mixed, they become yellow, and acquire the power of readily dissolving gold, which neither of the acids possessed separately. This mixture evolves chlorine, a partial decomposition of both acids having taken place, and water, chlorine, and nitrous acid gas, are thus produced; that is, the hydrogen of the muriatic acid abstracts oxygen from the nitric to form water: the result must be chlorine and nitrous acid.†

Aqua-Regia.

For every 101 parts in weight of real nitric acid (equivalent to 118 of hydro-nitric acid) which are decomposed, 67 parts of chlorine, Sir H. Davy calculates, are produced. According to this view it is not correct to say that *aqua regia* oxidates gold or platinum, since it merely causes their combination with chlorine. By long continued and gentle heat, nitro-muriatic acid may be entirely deprived of chlorine, and it then loses its power of acting on gold and platinum. H. 1. 325.

Action on gold.

514. *Nitrogen and Chlorine—Chloride of Nitrogen*.—These gases do not unite *directly*, but the compound may be

Chloride of Nitrogen.

* *Ann. de Chem.* xxxv. 80.† Davy, *Journal of Science and the Arts*, vol. i. p. 67.

obtained by exposing a solution of *nitrate* or *muriate of ammonia* to the action of chlorine, at a temperature of 60° or 70° . The gas is absorbed, and an oil-like fluid, heavier than water, is produced. It is the most powerfully detonating compound with which we are acquainted. It was discovered by M. Du-long, in 1812.*

Process for
obtaining,

The simplest mode of obtaining this compound, consists in filling a perfectly clean glass basin with a solution of about one part of sal-ammoniac in twelve of water, and inverting into it a tall jar of chlorine. The saline solution is gradually absorbed and rises into the jar, a film forms upon its surface, and it acquires a deep-yellow colour; at length small globules, looking like yellow oil, collect upon its surface, and successively fall into the basin beneath, whence they are most conveniently removed by drawing them into a small and perfectly clean glass syringe, made of a glass tube drawn to a pointed orifice, and having a copper wire with a piece of clean tow wrapped round it for a piston; fig. 101, in this way a globule may be drawn into the tube, and transferred to any other vessel.

Pl iv.

Properties.

515. Its specific gravity is 1,653 water being 1,† it is not congealed by cold. Its odour is irritating and peculiar; it very soon evaporates when exposed to air. This substance is decomposed with violent detonation by many combustibles, especially phosphorus, and fixed oils. Its discoverer, M. Du-long, was severely wounded in his first experiments on it; and Sir H. Davy had a serious injury done to his eyes in repeating them.

Precautions
in experi-
menting with.

In making these experiments, a small globule of the compound, about the size of a mustard-seed, should be cautiously transferred to a clean porcelain basin, half filled with water. The basin should be covered with a wire safe-guard. A very small piece of phosphorus, fixed to the end of a long rod with the extremity dipped in oil may be then brought into contact with the globule, which instantly explodes, dispersing the water, and breaking the basin. At 160° it distils without change, but between 200° and 212° it explodes, and is decomposed. It was submitted to the action of 125 different substances, by Messrs Porret and Wilson, from which it appears that mere contact with many combustible substances causes explosion at common temperatures.

The metals, resins, and sugar did not cause it to explode.‡

Composition
of chloride of
nitrogen.

516. It yields, by decomposition, 1 volume of nitrogen and 4 of chlorine; and as the specific gravity of nitrogen to chlorine is as 14 to 36,0, so it may be said to consist of 1 proportional of nitrogen + 4 proportionals of chlorine, or $14 + \frac{4 \times 36}{14}$, by weight, and its number will be 158.

* *Annales de Chimie*, vol. lxxv.

† *Phil. Trans.* 1813.

‡ *Nicholson's Journal*, vol. xxxiv.

| Nitrogen. | Chlorine. |
|-----------|-----------|
| 14 | 36 |
| | 36 |
| | 36 |
| | 36 |

517. In the state of vapour, it is probable that the five volumes of æriform matter which it affords by decomposition are condensed into one, since its decomposition by mercury is not attended by any change of its volume.

518. *Nitrogen and Iodine.*—*Iodide of Nitrogen.*

144 *Nitrogen.*—A compound of these bodies may be procured by pouring a solution of ammonia upon a very small quantity of iodine. Hydriodic acid is one product, and the other a brown powder, which detonates upon the slightest touch, and is resolved into nitrogen and iodine. It

may be collected by pouring off the liquid, and placing it, while moist, in small parcels upon bibulous paper, where it must be suffered to dry spontaneously.

If we collect the powder on two or more separate pieces of paper, and place them at several inches apart, the explosion of any one of them will, sometimes, cause that of the others. Exp.

When it detonates, the purple fumes of iodine are perceptible.

When left exposed it gradually evaporates. It often explodes spontaneously.

According to the experiments of M. Colin the iodide of nitrogen consists of 1 atom of nitrogen + 3 atoms of iodine.

519. *Nitrogen and Hydrogen—Ammonia; or Volatile alkali.*—Ammonia in its purest form exists in the state of a gas. Ammonia or volatile alkali.

It may be obtained by heating a mixture of *quicklime* and *muriate of ammonia* (*Sal ammoniac*.) Two parts of dry quicklime and one of muriate of ammonia, each separately powdered, may be introduced into a small glass retort, or gas bottle, and upon the application of a gentle heat the gas passes over. It must be received over mercury. Process for obtaining

520. Persons not having a mercurial apparatus may receive this gas in a glass jar inverted over a tube bent as in fig. 102. Pl. 5. As the gas is evolved from the materials contained in the gas-bottle, it rises into the jar and displaces the atmospheric air. When the jar is filled with ammonia (which will be known by its pungent odour as it escapes from the neck of the jar) the tube may be carefully withdrawn, and a well ground stopper be inserted into the neck of the jar.

521. Ammonia is permanently elastic at common temperatures and pressures. At the temperature of 50° F. and under a pressure of 6.5 atmospheres it becomes a transparent colourless liquid.* Its refractive power in this state surpasses that of water itself and its specific gravity is 0.76. Properties.

* Faraday, *Phil. Trans.* 1823, p. 196.

522. Its odour is extremely pungent and acrid, but when diluted by mixture with common air, agreeably stimulant. It converts most vegetable blues to green and the yellows to red, properties which belong to the bodies called *alkalies*. Ammonia, therefore, has been termed *volatile alkali*.

Does not support combustion. 523. It extinguishes flame, and is fatal to animals. Before, however, a candle is extinguished by immersion in this gas, the flame is enlarged, by the addition of another of a pale yellow colour, which descends from the mouth to the bottom of the jar. If the flame of the candle be only in part immersed in the gas, this yellowish flame rises a few lines above the other.

May be inflamed in oxygen gas. 524. Ammoniacal gas is not sufficiently inflammable to burn when in contact with common air. But, when expelled from the extremity of a pipe, having a small aperture, surrounded by oxygen gas, it may be kindled, and it then burns with a pale yellow flame, the products of its combustion being water and nitrogen gas.

Absorbed by water. 525. Ammonia is rapidly absorbed by water.* A drop or two of water being admitted to a jar of this gas, confined over mercury, the gas will be immediately absorbed, and the mercury will rise, so as to fill the whole of the jar, provided the gas be sufficiently pure. Ice produces the same effect in a still more remarkable manner, and liquid ammonia is produced.

Exp. Specific gravity. 526. Its specific gravity to hydrogen is as 8,5 to 1; 100 cubical inches weighing 18 grains, B. Air being = 1 its specific gravity is 0,59027. Oxygen = 1 it is 0,53125, and 100 cubic inches weigh 18,0035. T.

Exp. 527. When ammonia is presented to muriatic acid it unites with it and white vapours, composed of muriate of ammonia are formed. This will be evident if we moisten the inside of a glass jar with muriatic acid, and pass into it a small quantity of ammonia, dense clouds of muriate of ammonia will immediately form (37).

Liquor ammonia. 528. The usual state in which ammonia is employed is in solution, both in chemistry and medicine. This solution bears the name of Liquor Ammonia of the London Pharmacopœia.† It may be obtained by passing the gas into water in a proper apparatus, fig. 81, or by distilling over the water and gas together.

Mr Phillips's process. The following process, recommended by Mr Phillips, answers well. On 9 ounces of well burned lime pour half a pint of water, and when it has remained in a well closed vessel for about an hour, add 12 ounces of muriate of ammonia in powder and three pints and a half of boiling water; when the mixture has cooled, pour off the clear portion, and distil from a retort 20 fluid ounces. The specific gravity of this solution, which is sufficiently strong for most purposes, is 0,954.‡

* According to Dr Thomson water takes up 780 times its bulk.

† Aqua Ammonia of the United States Pharmacopœia.

‡ Remarks on London Pharmacopœia, p 34.

The specific gravity of the officinal solution directed in the *Pharmacopœia*, is 0,960.

529. Liquid ammonia should be preserved in well-stopped glass bottles, since it loses ammonia and absorbs carbonic acid, when exposed to air. When heated to about 140° , ammonia is rapidly given off by it; when concentrated it requires to be cooled to -40° before it congeals, and then it is apparently inodorous.

530. Dr Henry* first observed that a mixture of ammonia and oxygen gas might be fired by an electric spark, and this property furnishes a means of analyzing the alkaline gas. Electricity also decomposes ammoniacal gas. If a succession of electrical sparks be passed through a small portion of the gas confined in a proper tube over quicksilver, it will increase to about twice its original bulk, and lose its easy solubility in water. If the gas thus expanded be mixed with from one-third to one-half its bulk of oxygen, and an electric spark passed through the mixture, an explosion takes place, attended by considerable diminution. Note the amount of the diminution, divide it by 3, and multiply the product by 2. The result shows the quantity of hydrogen.

Suppose, for example, that we expand 100 measures of ammonia to 200; and that, after adding 80 measures of oxygen gas, we find the whole (= 280 measures) reduced by firing to 55 measures; the diminution will be 225. Dividing 225 by 3, we have 75, which, multiplied by 2, gives 150 measures of hydrogen gas from 100 of ammonia. Deducting 150 from 200, we have 50 for the nitrogen gas contained in the product of electrization. Therefore 100 measures of ammonia have been destroyed, and expanded into

150 measures of hydrogen gas = 3 volumes.

50 ————— nitrogen gas = 1 volume.

531. If hydrogen be made the decimal unit and the three volumes of hydrogen in ammonia represent 3 atoms, and the 1 vol. of nitrogen 1 atom, the weights of the atoms of hydrogen and nitrogen will be as their specific gravities, viz. as, 0694 to 9722 or as 1 to 14, and the annexed symbols will represent the composition and volume of ammonia: H. 1. 410.

| | | | |
|----------------|---------------|-----|----------------|
| Nitrogen 14 | Hydrogen 1 | =17 | Ammonia. 17 |
| | Hydrogen 1 | | |
| | Hydrogen 1 | | |

480. When ammonia and oxygen are detonated, the nitrogen is oxidized as well as

the hydrogen; hence, if excess of oxygen be used, the whole of the ammonia disappears, and nitrate of ammonia is formed.

532. Ammonia is decomposed by passing it through a red-hot iron tube; it suffers expansion, and is resolved into hydro-

How preserved.

Analysis of ammonia

Exp:

Example:

Atomic weight.

Composition.

Decomposed by a red heat.

* *Phil. Trans.* 1809.

gen and nitrogen gases, furnishing a singular instance of change of properties in consequence of chemical combination. *a* fig. 103, is a bladder filled with ammonia which may be passed through the iron tube *b*, placed in the furnace *c*; the gas is decomposed, and hydrogen and nitrogen may be collected over the water in *d*.

Pl. v.

Synthesis.

533. Ammonia is produced synthetically during the decomposition of many animal substances; it is also formed during the violent action of nitric acid upon some of the metals; and by moistened iron-filings exposed to an atmosphere of nitrogen; in these cases the nascent gases unite so as to form a portion of ammonia.

Salts of ammonia.

534. Ammonia combines with the acids, and produces a class of salts which, with very few exceptions, are soluble in water, and which evolve the odour of ammonia when mixed with lime or with pure potassa. These salts are, for the most part, entirely dissipated, and, generally speaking, decomposed by heat.

Decomposed by chlorine.

535. *Ammonia and Chlorine*—No compound of chlorine and ammonia can exist, for as soon as ammonia is brought into contact with chlorine, it is decomposed. On mixing 15 parts of chlorine and 40 of ammonia, 5 parts of nitrogen are liberated and muriate of ammonia is formed. *B.**

Phenomena attending.

When the two gases are suddenly mixed they act upon each other so powerfully as sometimes to produce detonation.

Exp.

Invert a matrass with a conical neck and wide mouth, over another with a taper neck containing a mixture of sal-ammoniac and lime, heated by a lamp. As soon as the upper vessel seems to be full of ammonia, by the overflow of the pungent gas, it is to be cautiously lifted up, and inserted, in a perpendicular direction, into a wide mouthed glass decanter or flask, filled with chlorine. On seizing the two vessels thus joined, with the two hands, covered with gloves, and suddenly inverting them, like a sand-glass, the heavy chlorine and light ammonia, rushing in opposite directions, unite, with the evolution of flame. U. 158.

Sal-ammoniac.

536. *Ammonia and Muriatic Acid—Muriate of Ammonia—Hydrochlorate of Ammonia—Sal-Ammoniac.*—This salt may be produced directly by mixing equal volumes of ammonia and muriatic acid, over mercury, when an entire condensation ensues (48) and a white solid is formed.

Pl. iii.

This may be shown by means of the apparatus fig. 53. Into one of the retorts a small quantity of muriatic acid, (or the materials from which the acid gas is usually obtained (418), is

Chlorate of ammonia.

* *Ammonia and chloric acid—Chlorate of Ammonia* is formed by saturating chloric acid with carbonate of ammonia. It forms very soluble acicular crystals, of a sharp taste, which detonate when thrown upon hot coals. It probably consists of 1 proportional of each of its components.

Iodate.

Ammonia and Bromine. Ammonia unites with its own volume of hydro-bromic acid gas, forming a white, solid, volatile salt, which is soluble in water, and crystallizes in long prisms by evaporation.

Iodate of Ammonia forms small indeterminate crystals; when heated they are decomposed into oxygen, nitrogen, water and iodine.—When heated in close tubes, the tubes are frequently burst; but Gay-Lussac succeeded in collecting the products, which were equal volumes of oxygen and azotic gases. He states its composition at 100 acid + 10,94 ammonia, or 2 vols. of gaseous ammonia, 1 volume of iodine in vapour, and 2½ volumes of oxygen. H. 414.

introduced ; and into the other liquid ammonia (or the mixture of lime and muriate of ammonia (519). The evolved gases passing into the cylinder unite, producing dense clouds of muriate of ammonia which concrete upon the inner surface of the cylinder.

537. It is easy to calculate the composition of this salt, for since 100 cubic inches of muriatic acid gas weigh 39 grains* and the same volume of ammonia weighs 18,18 grains,† muriate of ammonia must consist of

| | | Atoms. | |
|-------------------------|------------------|-------------|-------|
| Muriatic acid | 68,519 | 1 | 37 |
| Ammonia | 31,481 | 1 | 17 |
| | <hr/> | | <hr/> |
| | 100, | | 54 |

But in its ordinary state, the salt contains water, the proportion of which, according to Berzelius is, 19 parts in 100 of the salt,‡ but this does not agree with any atomic constitution, and it is probable, therefore, that the water is not essential to it, but accidental. H. 1. 416.

538. Muriate of ammonia when heated sublimes in the form of white vapour ; and may even be passed through glass or porcelain tubes heated to redness, without alteration.

539. It is readily soluble in water, three parts and a half of which at 60°, take up one of the salt. During its solution much caloric is absorbed It is still more soluble in boiling water, from which it crystallizes on cooling. It slightly attracts moisture from the air On the addition of a solution of pure potassa, soda, or lime, the alkali is disengaged, as is evinced by the pungent smell that arises. This may be proved by rubbing together in a mortar muriate of ammonia and quicklime.

540. Though generally considered as a neutral salt, yet, if placed on litmus paper and moistened, Berzelius observes, that the paper is reddened after some moments, as it would be by an acid.

541. It is decomposed by baryta, strontia, lime and magnesia. H.

542. Muriate of ammonia was formerly imported from Egypt, where it was obtained by burning the dung of camels ; it is now abundantly prepared in various parts of Europe by several processes. The most usual method is to decompose sulphate of ammonia by the muriate either of soda, or of magnesia. The sulphate of ammonia may be procured for this purpose, from the soot of coal ; or by digesting the impure carbonate of ammonia, procured by exposing bones and other animal matters to

* 39,1839 } air = 1. Thomson's First Prin.
† 18,0035 }

‡ 80 Ann. de Chim. 253.

a red heat, with sulphate of lime. In commerce it usually occurs as procured by sublimation, in white cakes, hard and somewhat elastic, and in this compact state it requires for solution 3,25 parts of water at 60°.

Uses. 543. Sal-ammoniac is used in the arts for a variety of purposes, especially in certain metallurgic operations. It is used in tinning, to prevent the oxidation of the surface of copper; and small quantities are consumed by dyers. Dissolved in nitric acid, it forms the *aqua regia* of commerce, used for dissolving gold, instead of a mixture of nitric and muriatic acids (513.)

Native. 544. *Native Muriate of Ammonia* occurs massive and crystallized, in the vicinity of volcanos, and in the cracks and pores of lava near their craters. It has thus been found at Etna, and at Vesuvius, in the Solfaterra near Naples, and in some of the Tuscan Lakes. An efflorescence of native sal-ammoniac is sometimes seen upon pit-coal. Its colour varies from the admixture of foreign matter, and it is frequently yellow from the presence of sulphur. It is said that considerable quantities of native sal-ammoniac are also found in the country of Bucharria, where it occurs with sulphur in rocks of indurated clay. The ancients, according to Pliny, called this salt *ammoniac*, because it was found near the temple of Jupiter Ammon, in Africa.*

Origin of the name.

Nitrate of ammonia.

545. *Ammonia and Nitric Acid*--*Nitrate of Ammonia*.—This salt may be procured by the direct union of ammonia with nitric acid; or more easily, by saturating dilute nitric acid with carbonate of ammonia. It has long been known, and was formerly called *Nitrum flammans*. It differs in form according to the manner in which its solution has been evaporated; if at a temperature below 100°, its crystals are six-sided prisms terminated by six-sided pyramids; if boiled down, its crystals are thin and fibrous; and when the evaporation is carried so far that the salt immediately concretes on a glass rod by cooling, it then forms a compact and shapeless mass. It has been mentioned as the source of nitrous oxide, and when heated is entirely resolved into that gas and water.† ‡ The dry salt consists of one proportional of nitric acid = 54 + one proportional of ammonia =

Hydriodate of ammonia.

* *Hydriodate of Ammonia*.—In a former paragraph (518) the action of iodine on ammonia has been stated to produce a portion of hydriodate of ammonia: this compound may be directly formed by mixing equal volumes of hydriodic and ammoniacal gases; or by saturating liquid hydriodic acid by carbonate of ammonia; it forms very soluble and deliquescent cubic crystals, volatile in close vessels without decomposition.—Gay-Lussac, *Annales de Chim.* xci.

† One pound of the compact kind gives, by careful decomposition, nearly five cubic feet, or rather more than 34 doses. H.

‡ Its specific gravity compared with water, is 1,5785. (Fourcroy.)

17, and therefore the representative number of nitrate of ammonia is 71.*

546. The solubility of nitrate of ammonia varies, according to the temperature in which it has been formed. When in crystals, it requires twice its weight of water for solution, or half its weight of boiling water. It deliquiates, in all its forms when exposed to the atmosphere. Its taste is acrid and bitter. It contains different proportions of water of crystallization; according to Berzelius, the prismatic variety affords 11,232 per cent.† According to Davy, the fibrous variety contains 8,2 per cent.; and the compact, obtained by evaporating the solution till it concretes, 5,7 per cent. of water of crystallization.‡

Solubility.

Proportions of water.

Atmospheric air.

547. Atmospheric Air.—The composition of atmospheric air has been frequently alluded to in the preceding pages, and as the student is now acquainted with its essential component parts, namely, oxygen and nitrogen, it may be right to consider its properties more at length.

Composition.

* Or it may be considered as containing two proportionals of nitrogen, three of hydrogen, and five of oxygen, as the following symbols show :

| Nitrate of Ammonia. | | | |
|---------------------|--------|----------|----------|
| Nitric Acid. | | Ammonia. | |
| 54. | | 17. | |
| Nitrogen | Oxygen | Nitrogen | Hydrogen |
| 14 | 8. | 14 | 1 |
| | 8. | | 1 |
| | 8. | | 1 |
| | 8. | | |
| | 8. | | |

Nitrous oxide consists of 1 proportional of nitrogen = 14 + 1 of oxygen = 8; hence the 2 proportionals of nitrogen in the salt (1 in the acid and 1 in the ammonia) will require 2 of oxygen to produce nitrous oxide, and the remaining 3 of oxygen will unite to the 3 of hydrogen, and form water; and accordingly nitrous oxide and water are the only possible results; so that the elements after the decomposition of the salt, are arranged thus :

Two proportionals of Nitrous Oxide.

| | |
|----------|--------|
| Nitrogen | Oxygen |
| 14 | 8. |
| | 8. |
| 14 | |

Three proportionals of Water.

| | |
|----------|--------|
| Hydrogen | Oxygen |
| 1 | 8. |
| 1 | 8. |
| 1 | 8. |

† 80 *Annales de Chimie*.

‡ Davy's *Researches*, p. 71.

Properties.

The atmosphere is a thin, transparent, invisible, and elastic fluid, which surrounds our planet and reaches to a considerable height above its surface, probably about 45 miles. It may be diminished in volume to a great extent by compression; according to Mr Perkins it becomes liquid under a pressure of 2000 atmospheres.*†

Weight.

548. That air is a ponderous body, was first suspected by Galileo, who found that a copper ball, in which the air had been condensed, weighed heavier than when the air was in its ordinary state of tension. The fact was afterwards demonstrated by Toricelli, whose attention was drawn to the subject by the attempt of a well-digger at Florence, to raise water by a sucking-pump to a height exceeding 33 feet. It was then found that the pressure of the atmosphere, and not nature's abhorrence of a vacuum, was the cause of the ascent of the water in the pump-pipe, and that a column of about the height mentioned was sufficient to equipoise the atmosphere.

Barometer.

549. In 1643, Toricelli filled a glass tube, three feet long and closed at one end, with quicksilver, and inverted it in a basin of the same fluid; he found that the mercury fell about six inches, so that the atmosphere appeared capable of counterbalancing a column of mercury 30 inches in height. The empty space, in the upper part of the tube, has hence been called the *Toricellian vacuum*, and is the most perfect that can be formed.

Pascal and Toricelli afterwards observed, that upon ascending a mountain, the quicksilver fell in the tube, because there was less air above to press upon the surface of the metal in the basin; and thus a method of measuring the heights of mountains by the *barometer*, as the instrument is now called, was devised. Sir Henry Englefield has constructed a barometer, expressly for these investigations, the mode of using which is described in the *Journal of Science and the Arts*, vol. v. p. 229.

Density of the atmosphere indicated.

550. The barometer indicates, by its rise and fall, a corresponding change in the density of the atmosphere. At the surface of the earth the mean density or pressure is considered equal to the support of a column of quicksilver 30 inches high.‡

Air-pump.

551. The general mechanical properties of the air are best illustrated by the *air-pump*, the construction of which much

* *Phil Trans* 1826.

† See Dr Wollaston "on the Finite extent of the Atmosphere"—*Bost Jour.* I. 15.

| | Inches. |
|--|---------|
| ‡ At 1000 feet above the surface the column falls to | 28.91 |
| 2000 | 27.86 |
| 3000 | 26.85 |
| 4000 | 25.87 |
| 5000 | 24.93 |
| 1 Mile | 24.67 |
| 2 | 20.29 |
| 3 | 16.68 |
| 4 | 13.72 |
| 5 | 11.28 |
| 10 | 4.24 |
| 15 | 1.60 |
| 20 | 0.95 |

resembles that of the common sucking-pump used for raising water, excepting that all the parts are more accurately and nicely made, the object being to exhaust the air as completely and expeditiously as possible.*

552. The specific gravity of atmospheric air, at mean temperature and pressure, that is, the thermometer being at 60° , and the barometer at 30 inches, is, usually considered as = 1. It is about 828,59 times as light as its bulk of water, 100 cubical inches weighing rather more than 30 grains. (30,5 H.)

Specific gravity.

553. Atmospheric air has already been stated to consist essentially of oxygen and nitrogen gases (547): whether it should be considered a mere mixture or a chemical compound is a question which has been much discussed. The recent experiments of M. Dulong have shown that the refractive power of the atmosphere is precisely such as a mixture of oxygen and nitrogen ought to have, and different from what would be expected were its elements chemically united.† The oxygen seems to be the only ingredient on which the effects of the air, as a chemical agent, depend. Hence combustible bodies burn in atmospheric air, only in consequence of the oxygen gas which it contains; and when this is exhausted, air is no longer capable of supporting combustion. Its analysis is satisfactorily demonstrated by the action of heated mercury, but the process is extremely tedious.‡ By exposure, during 12 days to mercury heated in a retort, a given quantity of atmospheric air was found to be diminished in bulk, and to have lost its property of supporting combustion. The mercury was changed into red scaly particles, and it had acquired an increase of weight. When these red particles were submitted to heat, in a retort, oxygen gas was evolved equal in bulk to what the air had lost in the first part of the experiment.

Chemical effects dependant on oxygen.

Lavoisier's experiments.

554. If a little sulphur or phosphorus be burnt in a jar of atmospheric air, instead of oxygen gas the combustion will be less vivid, and will cease sooner. The remaining air will not support combustion, and will be found to be nitrogen gas.

There are various ways of learning the proportion which the oxygen bears to the nitrogen; and as the relative fitness of the air for breathing has sometimes been considered as depending upon the quantity of oxygen contained in a given volume, the instruments used in these experiments have been called *eudiometers*.

Eudiometry.

555. From facts already stated it is obvious, that if atmospheric air, mixed with a certain quantity of hydrogen, be detonated by the electric spark the absorption will be proportionate to the quantity of oxygen present.

When 100 measures of pure hydrogen are mixed with 100 of pure oxygen, the diminution of bulk after detonation will amount to 150 parts, that is, one volume of oxygen requires

* See Camb. *Mechanics*, page 403.

† See M. Dulong's paper on "the refractive power of elastic fluids," in Brewster's *Journal*, vol. 4, p. 211.

‡ See Lavoisier's *Elements*, chap. iii.

Pl. iv.

for its saturation two of hydrogen. If we introduce into the graduated detonating tube (fig. 88) 300 measures of common air, and 200 of pure hydrogen, there will remain, after detonation 305 measures; so that 195 measures will have disappeared, of which one-third may be estimated as pure oxygen; hence 300 parts of air have thus lost 65 of oxygen, or about 21 *per cent.*

General rule.

556. The general rule, therefore, for estimating the purity of air by hydrogen gas may be stated as follows:—Add to 3 measures of the air under examination 2 measures of pure hydrogen; detonate; and, when the vessel has cooled, observe the absorption; divide its amount by 3, and the quotient is the quantity of oxygen.

Purity of other gases ascertained.

557. Upon the same principle, detonation of mixtures of oxygen and hydrogen is often resorted to, with a view of ascertaining the purity of those gases. Thus, suppose 100 measures of oxygen, and 300 of hydrogen, to be reduced by detonation to 130, the whole diminution will be = 270, which, divided by 3, gives 90 for the quantity of oxygen; so that it contained 10 *per cent.* of some gas, not condensable by detonation with hydrogen.

To ascertain the purity of hydrogen, it may be detonated with excess of pure oxygen. Thus, if we add 100 of pure oxygen to 100 of hydrogen, and detonate, there will be a diminution equal to two-thirds, or 150 parts if the hydrogen be pure. If, however, we suppose 100 of pure oxygen, mixed with 100 of hydrogen, to produce, after detonation, a residue of 80 measures; the diminution will then have been only 120 measures, of which two-thirds, or 80 measures, are hydrogen; so that the inflammable gas will have contained 20 *per cent.* of some other gaseous body, not condensable by detonation with hydrogen.*

Eudiometer of Volta.

558. This mode of ascertaining the purity of atmospheric air was first resorted to by Volta, and it is susceptible of great accuracy, since pure hydrogen and pure oxygen are easily procured. An improved detonating tube for these purposes has been described by M. Gay-Lussac.†‡ Several new Eudiometers have

* For a particular description of several points in eudiometry, see Faraday's *Chem. Manip.* sect. xvii. paragraph 919, &c.

† *Annales de Chem. et Phys.* iv. 188.

Dr Ure's eudiometer.

‡ In the eudiometer of Dr Ure, the atmospheric air, the most elastic and economical of all springs, is employed to receive and deaden the recoil. This eudiometer consists of a glass syphon (fig. 107), having an interior diameter of from 2-10ths to 4-10ths of an inch. Its legs are of nearly equal length, each being from six to nine inches long. The open extremity is slightly funnel-shaped, the other hermetically sealed; and has inserted near it, by the blow-pipe two platinum wires. The outer end of the one wire is incurvated across, so as nearly to touch the edge of the aperture; that of the other is formed into a little hook, to allow a small spherical button to be attached to it when the electrical spark is to be transmitted. The two legs of the syphon are from one-fourth to one-half inch asunder. The sealed leg is graduated by introducing successively equal weights of mercury from a measure glass tube. Seven ounces troy and 66 grains, occupy the space of a cubic inch; and 34 1-4 grains represent $\frac{1}{100}$ part of that volume. The other leg may be graduated also, though this is not necessary.

Pl. v.

To use this instrument, we first fill the whole syphon with mercury or water; the open leg is then plunged into a pneumatic trough, and any convenient quantity of the gases is introduced from a glass

been described by Professor Hare in the *American Jour. of Science*, Vols. II and X.

559. Scheele, in his eudiometrical experiments, employed *Of Scheele.*
sulphuret of potassa, the solution of which rapidly absorbs oxygen, as may be shown by agitating it with some atmospheric air, in a graduated glass tube. Or take two tubes, each a few inches long, closed at one end, and divided into 100 aliquot parts. Fill the one with atmospherical air, the other with oxygen gas, and invert them in two separate cups, filled with a solution of sulphuret of potassa. The sulphuret will ascend gradually within the tube of common air, till, after a few days, about four-fifths of its original volume will remain; but in that containing oxygen, it will ascend much higher, and, if the gas be pure, will even absorb the whole.

The explanation of this fact is, that liquid sulphuret of potassa has the property of absorbing oxygen, but not nitrogen. It therefore acts on atmospheric air, only as long as any oxygen gas remains, and may be employed as a means of ascertaining the quantity of this gas in the atmosphere at different times and at distant places. H. 1. 292.

560. The best instruments for these experiments are the eudiometric tubes of Dr Hope* and Dr Henry.† The former, *Of Hope.*
 fig. 104, consists of a small bottle, holding about three ounces, into which the glass tube *a*, which holds precisely a cubic inch, *Pl. v.*
 and is divided into 100 equal parts, is carefully fitted by grinding. It also has a ground stopper at *b*. To use it, the phial is filled with the solution of the alkaline sulphuret (which is best prepared by boiling a mixture of quicklime and sulphur with water, filtering the solution, and agitating it for some time in a bottle half filled with common air,) and the tube *a*, containing the air to be examined, fitted into its place. After

measure tube containing them in determinate proportions. Applying the finger to the orifice we next remove it from the trough, like a simple tube, and by a little dexterity transfer the gas into the sealed leg of the syphon. When we conceive enough has been passed up, the finger is removed and the mercury brought to a level in both legs, either by the addition of a few drops, or by the displacement of a portion, by thrusting down into it a small cylinder of wood. We now ascertain, by careful inspection, the volume of included gas. Applying the forefinger again to the orifice, so as also to touch the end of the platinum wire, we then approach the pendent ball or button to the electrical machine, and transmit a spark, but a slight push or pressure on the tip of the finger is felt, even when the gas is in considerable quantity and of a strongly explosive power. After explosion on gradually sliding the finger to one side and admitting the air, the mercurial column in the sealed leg will rise more or less above that in the other. The equilibrium is then restored by adding mercury, when we read off, without any reduction, the true resulting volume of gas. As two inches or more of air should always be left between the finger and the mercury, this atmospheric column serves as a perfect recoil spring, enabling us to explode very large quantities without danger.

We may analyze the residual gaseous matter, by introducing, either a liquid or solid reagent. We first fill the open leg nearly to the brim with quicksilver, and then place over it the substance whose action on the gas we wish to try. If liquid, it may be passed round into the sealed leg among the gas; but if solid the gas must be brought round into the open leg, its orifice having been previously closed with a cork or stopper. After a proper interval the gas having been transferred back into the graduated tube, the change of its volume may be accurately determined.—Ure's *Dict.* 440—Edin. *Phil. Trans.* 1818.—See, also, *Faraday*, p. 434.

* Nicholson's *Journal*, vol. iv.

† *Elements*, vol. i. p. 290

inverting and agitating the instrument, the stopper *b* may be opened under water, and the absorption is shown by the rise of the fluid in the tube. For the glass bottle Dr Henry substituted the elastic gum bottle *b*, fig. 105, in the neck of which a short piece of glass tube is secured, into which the tube *a* is fitted by grinding.

Pl. v.

Of Pepys.

In the *Philosophical Transactions* for 1807, Mr Pepys has described a modification of this Eudiometer, which may be often advantageously employed in delicate experiments, and by which an absorption of only $\frac{1}{1000}$ parts of the gas under examination may be measured.

Of Priestley.

561. When nitric oxide gas and atmospheric air are mixed, there is a production of nitrous acid, in consequence of the union of oxygen with the oxide (478); and if the mixture be made over water, an absorption, proportional to the quantity of nitrous acid formed, ensues. Upon this principle nitric oxide may be used in eudiometrical experiments, and, if proper precautions be attended to, it furnishes tolerably accurate results. Dr Priestly and Mr Cavendish* availed themselves of this mode, and Mr Dalton has offered some remarks upon its relative accuracy.†‡

Of Davy.

Sir H. Davy suggested the use of a solution of sulphate of iron, impregnated with nitric oxide gas, for the absorption of oxygen; it may be employed in the same way as the alkaline sulphuret (507.)

Pl. v.

562. If a stick of phosphorus be confined in a portion of atmospheric air it will slowly absorb the oxygen present. The rapid combustion of the same substance may also be conveniently resorted to. For this purpose a small piece of phosphorus may be introduced into the bulb of the tube *a*, fig. 106, containing a given measure of the air to be examined, confined over mercury, which, to prevent loss by expansion, should be suffered to occupy about half the tube, or to stand at *b*. The phosphorus may then be inflamed in the tube; and when the combustion is over and the tube cold, the residuary air may be transferred for measurement. These eudiometrical methods were used by Lavoisier, Berthollet, and Seguin§ and are both susceptible of accuracy, and a loss of volume of about 21 *per cent.* of the atmospheric air will invariably be found to have occurred.||

Of Lavoisier,
&c.

563. By experiments thus conducted, it has been found that the composition of the atmosphere is extremely uniform in all

* *Phil. Trans.* 1783.† *Phil. Mag.* vol. xxviii.‡ For the details of this process see Henry's *Chemistry*, vol. i. p. 312, edit. 10th.§ *Annales de Chimie*, tom ix. and xxxiv.

|| Since the discovery of Professor Döbereiner, that platinum sponge (sub-oxide of platinum) causes the union of hydrogen and oxygen gases (379), it has been applied to the purposes of Eudiometry. The sub-oxide of platinum being formed into small balls with clay, and passed up into small graduated tubes containing the air to be examined, over mercury.—See *Boston Jour. of Philosophy*, &c. vol. i. p. 548, ii. 230, iii. 13.—Henry's *Chemistry*, i. p. 237.

parts of the world, and at all heights above its surface; and that it contains between 20 and 21 volumes of oxygen in 100.*

| | By Measure. | By Weight. |
|--------------------|--------------|-------------|
| Oxygen | 21 | 23,3 |
| Nitrogen | 79 | 76,7 |
| | <hr/> 100 | <hr/> 100,0 |

Though oxygen and nitrogen are the essential component parts of atmospheric air, it contains other substances, which, however, may be regarded as adventitious, and the quantity of which is liable to vary: of these, carbonic acid and aqueous vapour are the most important and constant. The quantity of the former may usually be considered as amounting to less than 1 per cent. Carbonic acid in air.

564. The presence of aqueous vapour in the atmosphere is shown in a variety of ways, but most easily by exposing to it certain deliquescent substances which liquefy and increase in weight, in consequence of its absorption; and as the gases in general, unless artificially dried, also contain vapour of water, it is necessary, in delicate experiments, and in ascertaining their specific gravity, to take this ingredient into the account, or to separate it by proper means, such as exposure to very deliquescent substances, among which fused chloride of calcium is especially useful. Water in air,

The quantity of water contained in air and gases is subject to variation. From the experiments of Saussure and Dalton, it appears that 100 cubic inches of atmospheric air at 57°, are capable of retaining 0,35 grains of watery vapour; in this state the air may be considered at its maximum of humidity: it would also appear that all the gases take up the same quantity of water when under similar circumstances, and that it consequently depends, not upon the density or composition, but upon the bulk of the gaseous fluid. its quantity.

We are indebted to Mr Dalton for some valuable information respecting the state in which water exists in air; from which it may be concluded that it is in the state of vapour, forming an independent atmosphere, mixed, but not combined with, or dissolved in the air.

565. *Hygrosopes* and *Hygrometers* are instruments which show the presence of water in the air, its variation in quantity, and its actual quantity existing in a given bulk of air at any given time. Saussure employs a human hair, which, by its dilatations and contractions in moisture and dryness, is made to turn an index; Deluc used a thin strip of whalebone in the same way; Wilson employed a rat's bladder, which is filled with mercury, and tied on a large thermometer tube, and by its dilatation and contraction causes the mercury to fall and rise in the tube, and thus to indicate changes in the moisture of the air. Hygrometers.

* Dr Henry, who has made numerous experiments on the analysis of atmospheric air, has not yet been able to decide whether it contains 20 or 21 volumes of oxygen in 100, the proportion being mostly between those two numbers. H. 1. 294, edit. 10.

Mr Daniell has constructed a hygrometer, which shows the constituent temperature of the moisture in the atmosphere, by its precipitation upon a cold surface; comparing this with the temperature of the atmosphere, the difference furnishes a datum for calculating the quantity of vapour in a given quantity of air, and affords indications usefully applicable to predicting change of weather.*

SECTION III. *Sulphur.*

Properties.

566. Sulphur, or brimstone, is a brittle substance, of a pale yellow colour; insipid and inodorous, but exhaling a peculiar smell when heated. Its specific gravity is 1,990.† It becomes negatively electrical by heat and by friction.

Sulphur is principally a mineral product,‡ and occurs crystallized; M. Mitscherlich has discovered two primary forms of sulphur. The one, which occurs in nature, is an octoëdron with a rhombic base; the other, produced by the slow cooling of fused sulphur, an oblique rhombic prism. Its crystals are in a high degree doubly refractive.

How obtained.

567. Massive sulphur is chiefly brought from Sicily; it occurs native, and is found associated with sulphate of lime, sulphate of strontia, and carbonate of lime; it is not uncommon among volcanic products.

568. Roll-sulphur is chiefly obtained from sulphuret of copper; which is roasted and the fumes received into a long chamber of brick-work, where the sulphur is gradually deposited: it is then purified by fusion, and cast into sticks. In this state, if grasped by the warm hand, it splits with a crackling noise.

Action of heat.

569. According to the recent experiments of M. Dumas§ the fusing point of sulphur may be considered as $226^{\circ},4$. Between 230° and 284° it is as liquid as a clear varnish, and of the colour of amber; at about 320° it begins to thicken, and acquire a red colour; on increasing the heat, it becomes so thick that it will not pour. This effect is most marked between 428° and 572° ; the colour being then a red brown. From 572° to the boiling point it becomes thinner, but never so fluid as at 248° .

When the most fluid sulphur is suddenly cooled, it becomes brittle, but the thickened sulphur, similarly treated, remains soft, and more soft as the temperature has been higher. In this state it is applied to taking impressions from engraved stones, &c.

* See *Quarterly Jour. of Science*, vols. viii. ix. x.

† Sp. gr. of sulphur vapour $\left\{ \begin{array}{l} 1,111 \text{ air} = 1 \\ 1, \text{oxygen} = 1. \end{array} \right\} \text{T.}$

‡ It is said to have been detected in several vegetables and in gum arabic.—Jameson's *Jour.* xiv. 172.

§ *Ann. de Chim.* xxvi. 83, and *Quart. Jour.* N. S. iv. 463.

570. Fused sulphur has a tendency to crystallize in cooling, and by good management regular crystals may be obtained. For this purpose several pounds of sulphur should be melted in a crucible; and when partially cooled, the outer solid crust should be pierced, and the crucible quickly inverted so that the fluid portion within may gradually flow out, on breaking the solid mass, when quite cold, crystals of sulphur will be found in the interior. Mr Faraday and M. Bellani* have found that fused sulphur will remain fluid at common temperatures, and solidify when touched by a fragment of sulphur or a thread of glass.

Crystallization of.

571. Sublimed sulphur, when examined by a microscope appears composed of minute crystals; it is always slightly sour, and hence, for some pharmaceutical purposes, is directed to be washed in hot water.

Crystallizes.

572. Sulphur is insoluble in water, but unites with it under favourable circumstances forming the white *hydrate of sulphur*, termed *Lac sulphuris*. It dissolves in boiling oil of turpentine. It is also soluble in alcohol if both substances are brought together in the form of vapour. The sulphur is precipitated from the solution by the addition of water.

Hydrate.

573. Sulphur, retains a portion of hydrogen so obstinately that it cannot be wholly freed from it either by fusion or sublimation. Sir H. Davy detected its presence by exposing sulphur to voltaic electricity, when some sulphuretted hydrogen gas was disengaged. The hydrogen, from its minute quantity, can only be regarded as an accidental impurity, and as not essential to the nature of sulphur.

Contains hydrogen.

574. The purity of sulphur may be judged of by heating it gradually upon a piece of platinum leaf; if free from earthy impurities, it should totally evaporate. It should also be perfectly soluble in boiling oil of turpentine.†

Test of the purity of sulphur.

575. *Sulphur and Oxygen*.—Sulphur forms two well defined compounds with oxygen; the sulphurous and sulphuric acids; two other compounds of sulphur and oxygen have also been described under the names of *Hyposulphurous* and *Hyposulphuric Acids*; but these can scarcely be said to exist, except in combination with bases. If they be admitted as distinct compounds, sulphur may be considered as susceptible of four states of combination with oxygen, and these compounds will consist respectively of

Unites with oxygen.

Sulphurous acid,

- 1 Sulphur + 1 Oxygen = Hyposulphurous acid.
- 1 Ditto + 2 Ditto = Sulphurous acid.
- 1 Ditto + 2,5 Ditto = Hyposulphuric acid.‡
- 1 Ditto + 3 Ditto = Sulphuric acid.

Sulphurous acid is a gaseous body, which may be obtained by several processes;

* *Quart. Jour. N. S.* iv. p. 469. † *Aikins' Dictionary*, Art. *Sulphur*.
‡ 2 Sulphur + 5 oxygen, (H.)

How obtained.

576. By burning sulphur at a low temperature, in common air, under a glass bell; and if slips of linen cloth, dipped in a solution of potassa, be exposed to the vapour, the alkali forms a combination with the sulphurous acid, which may afterwards be washed off and evaporated. The dry salt, distilled with liquid tartaric acid, gives sulphurous acid gas.

It is formed, exclusively, when sulphur is burned in dry oxygen gas. The gas, when restored to its original temperature, is found to be contracted $\frac{1}{12}$ th or $\frac{1}{15}$ th of its bulk; but this is probably owing to the hydrogen contained in sulphur, for there is every reason to believe, that oxygen gas, by becoming sulphurous acid, is not at all changed in volume. H. 1. 383.

Usual process.

577. As the acid obtained by burning sulphur in this way, is commonly mixed with more or less sulphuric acid, when sulphurous acid is wanted it is commonly made by abstracting part of the oxygen from sulphuric acid. This may be done in several ways. If chips of wood, straw, or cork, oil or other vegetable matters be heated in strong sulphuric acid, the carbon and hydrogen of those substances deprive the acid of a part of its oxygen, and convert it into sulphurous acid. Nearly all the metals, with the aid of heat, have a similar effect.

The best method of obtaining sulphurous acid gas, is by putting two parts of mercury and three of sulphuric acid into a glass retort, and then raising the heat; sulphurous acid gas is formed, and may be collected and preserved over quicksilver. Half an ounce of mercury is sufficient for the production of several pints of the gas.

Absorbed by water.

578. Water takes up rather more than 30 times its bulk of this gas, forming the liquid sulphurous acid, which when recently prepared, has a sulphurous astringent taste, but, by keeping, it acquires a sour flavour.

Bleaches.

The watery solution does not redden infusion of litmus, as acids in general do, but totally destroys its colour. Hence its use in bleaching several vegetable and animal products. Prepared by the combustion of sulphur, it is much used for bleaching cotton goods* and also for whitening silk and wool; in wine countries it is sometimes used to check vinous fermentation. It restores the colour of sirup of violets, which has been reddened by other acids.

Exp.

579. Vegetable blues are reddened by sulphurous acid previous to their being discharged.

Noxious.

A pleasing instance of its effect on colours may be exhibited by holding a red rose over the blue flame of a common match, by which the colour will be discharged wherever the sulphurous acid comes in contact with it, so as to render it beautifully variegated, or entirely white. If it be then dipped into water, the redness, after a short time will be restored. U. 110.

580. This gas has a suffocating nauseous odour, and an astringent taste; it extinguishes flame, and kills animals; it is exceed-

* *Quart. Jour. of Science*, iv. 196.

ingly deleterious to vegetables, even in very minute quantity and proportion.*

581. Sir H. Davy inferred from his experiments on the combustion of sulphur in dry oxygen gas† that 100 cubic inches of sulphurous acid contain 100 cubic inches of oxygen. According to Dr Thomson‡ sulphurous acid gas is just twice as heavy as oxygen; and the experiments of Davy and of Thenard correspond very closely with this result. It follows, therefore, that sulphurous acid consists of equal weights of sulphur and oxygen; and consequently that 100 cubic inches weigh 67,77 grains, and contain 33,888 grains of sulphur. This proportion is also established by the researches of Berzelius.§

582. Sulphurous acid suffers no change at a red heat, but if mixed with hydrogen, and passed through a red hot tube, water is formed and sulphur deposited; under the same circumstances, it is also decomposed by charcoal, by potassium and sodium, and probably by several other metals. Usos.

583. Sulphurous acid is converted to the state of sulphuric acid by restoring oxygen to it. Converted into sulphuric acid by receiving oxygen.

A mixture of oxygen and sulphurous acid gases, both perfectly dry, and standing over mercury, is not diminished by remaining in contact with each other during some months; but if a small quantity of water be added, the mixture begins to diminish, and sulphuric acid is formed. Or if water impregnated with sulphurous acid be exposed to oxygen gas in a tube, the oxygen in 10 or 14 days is imbibed and sulphuric acid formed. The same gases in a state of mixture, by the action of electricity or by being driven through a red-hot porcelain tube, afford sulphuric acid. The proportions required for mutual saturation are two measures of sulphurous acid and one of oxygen gas.

To a portion of water saturated with sulphurous acid gas add a little oxide of manganese, a substance that contains much oxygen loosely combined, the pungent smell of the water, and the other characteristics of sulphurous acid will soon disappear. H. 1. 385. Exp.

584. Mr Faraday, by producing sulphurous acid from mercury and concentrated sulphuric acid sealed up in a bent tube, obtained it in a liquid state. He describes it as very limpid and fluid, and quite colourless. Its refractive power appeared to be nearly equal to that of water. It does not solidify at a temperature of 0° F. When a tube containing it is opened, it does not rush out as with an explosion, but a portion of the liquid evaporates rapidly, cooling another portion so much as to leave it in a liquid state under common barometric pressure. It rapidly dissipates, however, without appearing in visible fumes, but with a strong odour of sulphurous acid, leaving the tube perfectly dry. A portion of the vapour collected over Liquefaction of sulphurous acid gas.

* See Dr Turner's experiments on the effect of gases on vegetables, Brewster's Jour. Jan. 1828.

† Elements, 273.

‡ Ann. of Phil. vol. xvi.

§ Ann. de Chim. et de Phys. vol. v.

mercury proved to be pure sulphurous acid gas. A piece of ice dropped into the fluid, instantly made it boil from the heat communicated to it. The specific gravity of liquid sulphurous acid is about 1.42, at 45° F. it exerts a pressure of about two atmospheres.*

Anhydrous
sulphurous
acid.

Process for
obtaining.

585. M. Bussy of Paris has given the following directions for the preparation of anhydrous sulphurous acid.

586. Equal parts of mercury and sulphuric acid are put into a small matrass, which is connected with a receiver having a long tube passing into a small flask. The receiver is to be surrounded with melting ice, in order to condense the water which passes over with the gas. The tube is filled with fragments of fused chloride of calcium, to absorb any aqueous vapour which may not have been condensed in the receiver. The flask should also be surrounded with melting ice or a freezing mixture. As the acid passes over it is condensed in the flask and appears in the liquid state.

Properties.

587. When obtained in this manner the liquid sulphurous acid has the following properties. It is colourless, transparent, of the specific gravity of about 1.45, and it boils at the temperature of 14° F.

588. When poured on the hand it produces a sharp cold, and completely evaporates. If poured, drop by drop into water, at the ordinary temperature it occasions a species of effervescence, owing to the volatilization of part of the acid, and the surface of the water is covered with ice.

With this acid Mr Bussy has found it easy to freeze mercury. The mercury is to be placed in a watch glass on the plate of the air pump, and the acid being added the receiver is quickly placed over it and exhausted (158). From 20 to 30 grains of mercury and as much acid may be employed.

589. It has also been applied to the liquefaction of chlorine and several other gases.†

Union with
ammonia.

590. When sulphurous acid is mixed in equal volume with ammonia, a yellowish salt is produced, which is a *sulphite of ammonia*, and which consists of 32 sulphurous acid + 17 ammonia. When formed by saturating liquid ammonia with sulphurous acid, it crystallizes in four and six-sided prisms, soluble in their own weight of water and having an acrid taste. It is deliquescent, and becomes a *sulphate* by exposure to air.

Sulphuric
acid.

591. *Sulphuric acid*.—This body was formerly obtained by the distillation of green vitriol, and called *oil of vitriol*. It is now procured, in this country, by burning a mixture of about 8 parts of sulphur and 1 of nitre in close leaden chambers containing water, by which the fumes produced are absorbed, and by evaporation the acid is procured in a more concentrated state. This improved method of preparing sulphuric acid was invented by Dr Roebuck, about the year 1746.‡ Sulphuric acid has

* *Phil. Trans.* 1823, p. 190.

† See *Boston Journal of Philosophy*, vol. ii. 359.

‡ *Parkes' Chemical Essays*, vol. ii.—*Brande's Prefatory History of Chemistry*, vol. i. p. 39.

been known ever since the time of Basil Valentine, who appears to have discovered it about the close of the 15th century.

592. Sulphuric acid, as usually met with, is a limpid, colourless fluid, of a thick and oily consistence, having a specific gravity of 1,84; it boils at 570° , and freezes at -15° , contracting at the same time considerably in its dimensions. But the temperature at which the diluted acid congeals is singularly modified by the quantity of water which it contains. At the specific gravity of 1,780 it freezes at 45° ; but if the density be either increased or diminished, a greater cold is required for its congelation.* Its boiling point diminishes with its dilution; acid of the specific gravity of 1,78, boils at 435° , and acid of the specific gravity of 1,650 boils at 350° .†

Properties.

It is acrid and caustic, and when diluted with water, produces a very sour liquid. When mixed suddenly with water, (53) considerable heat is produced. Four parts, by weight, of concentrated sulphuric acid, and one of water, when mixed together, each at the temperature of 50° Fahrenheit, have their temperature raised to 300° . The greatest elevation of temperature, Dr Ure finds to be occasioned by the sudden mixture of 73 parts by weight of strong sulphuric acid with 27 of water. This rise of temperature takes place because the affinity or capacity of the compound of acid and water for caloric, is less than that of the acid and water separately. A diminution of bulk also ensues; one measure of acid and one of water not occupying the space of two measures, but about $\frac{1}{75}$ th less. H. 1. 384.

593. It rapidly absorbs water from the atmosphere. Even at its boiling temperature, when it is concentrated, does not prevent its taking up moisture from the air; hence it cannot be concentrated so well in an open as in a close vessel, on which account, retorts of glass or platinum, are used for the last stage of its concentration by the manufacturers.

Imbibes moisture.

594 It chars animal and vegetable substances, and is apt to acquire a brown tinge from any small particles of straw, resin, or other matters that may accidentally have fallen into it.

595. In sulphuric acid 1 proportional of sulphur = 16, is combined with 3 of oxygen = 24, and, consequently, dry sulphuric acid is correctly represented by $16 + 24 = 40$. As it usually occurs, it may be called *hydrated sulphuric acid*. At the specific gravity of 1,848 it contains 1 proportional of dry acid = 40, and 1 of water = 9, and is represented by the equivalent 49.

Composition.

596. The strength of sulphuric acid is best judged of by saturating a known quantity with an alkali, and it may be assumed as sufficiently correct, that 100 grains of dry sub-carbonate of soda neutralize 92 grains of pure liquid sulphuric acid; or that

Method of determining the strength of sulphuric acid.

* Keir, *Irish Phil. Trans.* iv. 88.† Dalton's *Chem. Phil.* ii. 404.

100 grains of the acid requires 108, or 108,5 of the subcarbonate for saturation.* See *Alkalimetry*.

Effect of
chlorine.

597. Sulphurous acid gas is condensed into Sulphuric acid by admixture with chlorine gas; but not unless the gases are in contact with water. In the latter case, the hydrogen of the water unites with the chlorine, and the oxygen with the sulphurous acid.

Not affected
by dry nitrous
gas.

598. Dry nitrous acid gas is also inefficient on dry sulphurous acid; but when placed in contact with a small quantity of water, all these bodies act mutually and rapidly on each other; the nitrous acid gas yields a portion of its oxygen to the sulphurous acid, from whence result nitrous gas and sulphuric acid, which, both combining with water, form white flakes upon the inside of the vessel. These flakes are made up of congeries of small crystalline needles. Water, brought into contact with these crystals, dissolves the sulphuric acid, and the nitrous gas is liberated with effervescence. By means, therefore, of a small quantity of nitrous gas, we may transform a large quantity of sulphurous acid into sulphuric acid, provided the acid gas be mingled with half its volume of oxygen, or with an equivalent quantity of atmospheric air. The phenomena are beautifully exhibited by admitting, into an exhausted and dry glass balloon, first 30 measures of sulphurous acid, next 15 of oxygen, and then 5 of nitrous gas. No perceptible change takes place, till a little water is introduced, sufficient to moisten the inside of the vessel, when the small quantity of red nitrous acid, formed on adding the nitrous gas, disappears, and composes the crystalline substance already described. When those crystals have been deposited on the inside of the balloon, and a small quantity more of water is admitted, there is an immediate effervescence from the escape of nitrous gas, which, meeting with oxygen gas, again becomes nitrous acid, and this, acting upon the sulphurous acid, the same combinations ensue as before, and may be repeated as long as sufficient sulphurous acid and oxygen remain.

Exp.

Theory of the
formation of
sulphuric
acid.

599. It is by a series of operations of this kind, that the formation of sulphuric acid is effected in the ordinary process for preparing it. The nitric acid, present in the salt-petre, abandons part of its oxygen to one portion of the sulphur, which, becoming sulphuric acid, unites with the potassa of the nitre. At the same moment nitrous gas is set at liberty, which, with the oxygen present in the air of the chamber, composes nitrous acid gas. Another portion of sulphur is converted into sulphurous acid, which becomes sulphuric acid by depriving the nitrous acid

* Mr Dalton has published (*New System of Chemical Philosophy*, vol. ii. p. 404,) a Table, exhibiting the specific gravity and boiling point of the acid of various strengths.† See *Appendix*.

Dr Ure also has given several valuable tables relating to this subject, in his *Experiments to determine the Law of Progression, followed in the Density of Sulphuric Acid at different Degrees of Dilution*. (*Quarterly Journal of Science and the Arts*, vol. iv. p. 114.) An extremely useful table of this kind will also be found in Mr Parkes's *Essays* above quoted (vol. ii. p. 444.)

† It is sometimes of importance to the chemical artist to know the proportion not of *real acid*, but of *acid of commerce*, in diluted sulphuric acid of different specific gravities. An approximation to the true proportion may be obtained, by increasing the numbers indicating the real acid, one fourth. For example, acid of the specific gravity 1,200, contains (according to the table of Mr Dalton) 20 per cent. of real acid, which increased one fourth, gives 25 per cent. of acid, of sp. gr. 1, 849. H.

of oxygen, the latter acid being brought back to the state of nitrous gas. This gas, absorbing the atmospheric oxygen, again becomes nitrous acid, which changes a fresh portion of sulphurous into sulphuric acid. This theory was first suggested by M. M. Clement and Desormes. It has since been modified by Gay-Lussac, who supposes that nitrous acid, and not nitrous gas, is disengaged from nitrate of potassa. But even if this be admitted, the subsequent steps of the process are still explicable on the original theory, which satisfactorily explains why so small a proportion of nitre as one eighth is adequate to the conversion of sulphur into sulphuric acid, though, capable of supplying only a very small share of the oxygen essential to this change.* H. 1. 386.

* * The formation of sulphuric acid by the combustion of sulphur and nitre has been illustrated by Mr Brande as follows.

Sulphurous acid consists of

| | | | |
|-------------------------|------------------|----------|--------------------------|
| Sulphur vapour 16 | Oxygen 8 8 | } 16 ; = | Sulphurous acid 32 |
| | | | |

And nitrous acid contains

| | | | |
|----------------|--------------|----------|--------------------|
| Nitrogen 14 | Oxygen 8. | } 32 ; = | Nitrous acid 46 |
| | 8. | | |
| | 8. | | |
| | 8. | | |

hence every *two* portions of sulphurous acid require *one* of nitrous acid, which transfers *two* of oxygen, and passes back into the state of nitric oxide, sulphuric acid being, at the same time, produced.

The gases, therefore, before decomposition, may be thus represented :

| | | | | | |
|--------------------|--------------|------|-------------------|----------|--------------|
| 16 | Oxygen 8. | } 16 | } 32 | Nitrogen | Oxygen 8. |
| Vapour of sulphur. | 8. | | | 14 | 8. |
| | | | | 8. | |
| 16 | 8. | | | 8. | |
| Vapour of sulphur. | 8. | | | 8. | |
| | | | | | |
| | | | | | |
| Sulphuric acid. | | | Nitrous acid gas. | | |

And after decomposition as follows :

| | | | | | |
|-------------------------|--------------|------|------|----------------|--------------|
| Sulphur vapour 16 | Oxygen 8. | } 24 | } 16 | Nitrogen 14 | Oxygen 8. |
| | 8. | | | | 8. |
| | 8. | | | | 8. |
| Sulphur vapour 16 | Oxygen 8. | } 24 | | Nitric oxide. | |
| | 8. | | | | |
| | 8. | | | | |
| Sulphuric acid. | | | | | |

Analysis of
sulphuric
acid,

600. The decomposition of sulphuric acid may be effected by passing it through a red-hot platinum tube, when it is resolved into sulphurous acid, oxygen and water.

When heated with charcoal, sulphuric acid gives rise to the production of carbonic and sulphurous acids; with phosphorus it produces phosphoric and sulphurous acids; and, with sulphur, sulphurous acid is the only product. It is decomposed by several of the metals, which become oxidized, and evolve sulphurous acid, as shown in the production of this acid, by boiling sulphuric acid with mercury (577), tin, lead, &c.

by galvanism.

601. The liquid acid is also decomposed by platinum wires, communicating with the extremities of a galvanic pile. At the end of the negative wire, flocculi of sulphur appear, and at the positive end oxygen gas is evolved; and a brownish tint is produced by the formation, doubtless, of sulphate of platinum. (H.)

Uses.

602. Sulphuric acid is largely consumed in a variety of manufactures. It is used by the makers of nitric, muriatic, citric, and tartaric acids; by bleachers, dyers, tin-plate makers, brass-founders and gilders. For these purposes it is generally sufficiently pure as it comes from the wholesale manufacturer; but, as traces of lead, lime, and potassa, are usually found in it, it often requires to be purified by distillation for the use of the experimental chemist.*

Purification
of.

If the acid of commerce contain dissolved sulphate of lead, it becomes turbid on dilution, so that its remaining clear when mixed with water, is some proof of its purity, as far at least as lead is concerned.

Distillation
of sulphuric
acid;

The distillation of this acid in glass retorts requires some precaution, in consequence of the violent jerks which the production of its vapour occasions, and which often break the vessel; this may be prevented by putting some strips of platinum into the acid (152); it then boils quietly, and it is only necessary to take care that the neck of the retort and the receiver are not broken in consequence of the high temperature of the condensing acid.

To purify sulphuric acid, it must be distilled in a glass retort, placed in the sand-bed of a reverberatory furnace. This process requires considerable care. But to those who have sufficient experience in chemical operations, the instructions below may be useful; especially as it is indispensable, in all experiments of research, to employ an acid purified by distillation.†

* By evaporating 100 parts of sulphuric acid of commerce in a platinum dish, Dr Ure obtained from one half to three quarters of a grain of solid matter, consisting of about two parts of sulphate of potassa and one of sulphate of lead. Berzelius has found a minute quantity of titanium in sulphuric acid of English manufacture, and tellurium in acid prepared at Stockholm.* Selenium, also, has been met with in sulphuric acid prepared from pyrites. H. 1. 385.

* Thomson's *Annals*, x. 464.

† The furnace in which this process is conducted, should have a contrivance for supporting a sand-bath within it at a proper height; and an opening in the side, for transmitting the neck of the retort. The retort must be coated with clay and sand over its whole body, and also over that part of the neck which is exposed to the fire. It is then to be placed, the coating being previously dry, in the sand-

603. Sulphuric acid may be less perfectly purified by diluting it with an equal weight of water, allowing the impurities to settle, decanting the clear liquor and evaporating it to the proper degree in a glass retort.

604. Besides the sulphuric acid already described, there is another kind, called from the place where it has been long manufactured, the *Sulphuric acid of Nordhausen*. It is prepared by distilling the proto-sulphate of iron, and is much used in dissolving indigo. It has been investigated by Dr Thomson* and Mr Bussy.† Its colour is always dark, and it is opaque. Its specific gravity is 1,896. When exposed to the air, it smokes in consequence of its avidity for moisture. It boils at a temperature between 104° and 122° F. When heated in a glass retort, to which a receiver is luted surrounded by a mixture of snow and salt, one half of the acid passes over in a solid state, forming a snow-white acid which resembles asbestos. This is *anhydrous sulphuric acid*, or real sulphuric acid free from water. In the retort there remains a liquid acid consisting of 1 atom of acid and 1 atom of water, and agreeing, therefore with common oil of vitriol.

Glacial sulphuric acid.

Anhydrous sulphuric acid smokes strongly on exposure to the air, and is dissipated so speedily that it cannot be weighed. Dr Thomson has obtained it crystallized in flat rhomboids, quite transparent. It liquefies at about 66° F., and is then more fluid than common sulphuric acid, and has a high refractive power. At that temperature it has the specific gravity of 1,97.

When the solid acid is dropped into water, it combines with that liquid so violently as to make a noise resembling the quenching of a bar of red-hot iron. In the proportion of 2 atoms to 1 atom of water, it constitutes the Nordhausen acid, the atomic weight of which is therefore $80 + 9 = 89$. H. 1. 391.‡

bath, about one half filled with sulphuric acid; and a receiver must be applied, but not luted on. The fire must now be lighted, and raised with extreme caution. The first portion that comes over, amounting to about one sixth, consists chiefly of water, and may be rejected. This is followed by the concentrated acid; and, at this period, there is great risk that the neck of the retort will be broken, by the contact of the condensed acid, which has a very high temperature, and which frequently cracks the glass, as effectually as the application of a red-hot iron. The first must be regulated by the register door of the ash pit, so that several seconds may elapse between the fall of the drops into the receiver. The process may be continued as long as any acid is condensed. The retorts employed for this purpose, should be most attentively annealed.

The difficulty of rectifying sulphuric acid is much diminished by using a retort of the capacity of from two to four quarts, when a pint of the acid is employed, and by connecting its neck with the receiver by means of an adopter three or four feet long. The retort may be set over a charcoal fire, and the flame made to play gently on its bottom. No luting is to be employed, and the receiver is to be surrounded with cold water. With this arrangement, and a cautious regulation of the heat, Dr Ure finds that sulphuric acid may be distilled without much risk, in a continuous gentle stream.

* *System of Chemistry*, 6th edit. ii. 113 and *First Principles*, i. 214.

† *Ann. of Philos.* N. S. viii. 259.

‡ It has long been an object with the manufacturer to obtain sulphuric acid without the aid of nitre, and a patent has been obtained for a process of this kind, invented by Mr Hill. It consists in submitting coarsely-powdered iron pyrites (sulphuret of iron,) to a red heat, in cylinders communicating with a leaden chamber containing water; the sulphur, as it burns out of the pyrites, appears at once to pass into the state of sulphuric acid.

605. *Native Sulphuric Acid* has been found by Professor Baldassari, in the cavities of a small volcanic hill, called Zocolino, near Sienna, and by M. Humboldt in the water of the river Vinagre in the Andes of Popayan.*

Hypo-sulphurous acid.

606. *Of Hypo-sulphurous Acid*—This acid exists only in combination with salifiable bases, forming compounds which were first examined in 1813 by Gay-Lussac, and were called by him *sulphuretted sulphites*. Besides other methods of preparing these salts, he found that they might be obtained by digesting the solution of a sulphite with sulphur, an additional quantity of which might thus be made to combine with the sulphurous acid. It had also been long ago observed by Mr Higgins of Dublin, that liquid sulphurous acid dissolves iron without effervescence; and Berthollet afterwards showed that in this case the iron is oxidized at the expense of the sulphurous acid, and that sulphur is disengaged, which immediately unites with the sulphite of iron, forming a sulphuretted sulphite. Dr Thomson appears to have been the first who took a just view of these phenomena. The new compound he found to be a neutral salt, containing a peculiar acid of sulphur, to which he gave the name of *hypo-sulphurous acid*, and to its compounds that of *hypo-sulphites*. These compounds have been since examined with great ability by Mr Herschell, who has not, however, succeeded completely in his attempt to exhibit the acid in a separate state; nor indeed does it appear capable of existing permanently when uncombined with a base. From the experiments of Dr Thomson and Mr Herschell, it may be inferred to be a compound of 1 atom of sulphur + 1 atom of oxygen, and its representative number will be $16 + 8 = 24$.

Composition.

Hypo-sulphuric acid.

607. *Hypo-sulphuric Acid*.—This acid was discovered by Welter and Gay-Lussac in 1819.† Their process for forming it consists in passing a current of sulphurous acid through water, in which finely powdered peroxide of manganese is kept mechanically suspended. There is immediately produced a perfectly neutral solution consisting of hypo-sulphate and common sulphate of manganese.‡ When the solution is sufficiently concentrated, pure baryta is added to the previously heated liquor, and agitated along with it, taking care to employ an excess of the earth. All the oxide of manganese is thus separated; and, sulphate of baryta being insoluble, the filtered liquor contains only the hypo-sulphate and also the redundant portion of that earth. The latter is to be separated by a stream of carbonic acid, and subsequent ebullition to expel any excess of carbonic acid. The hypo-sulphate is then to be crystallized, dissolved in water and decomposed by just the quantity of sulphuric acid, which is required to precipitate the baryta. The filtered liquor is to be concentrated, by exposing it under the

* See *Boston Jour. of Philos.* vol. 11. p. 467.

† *Ann de Chim. et de Phys.* vol. 10.

‡ According to M. Heeren, the temperature should be low, and the largest portion of hypo-sulphuric acid is formed at the commencement of the operation.

exhausted receiver of an air-pump, along with a vessel of sulphuric acid, till it has attained the density of 1,347. If continued to be exposed, it is resolved into sulphurous acid which exhales, and sulphuric acid which remains liquid.

608. Oxygen gas, atmospheric air, chlorine, concentrated nitric acid, and red sulphate of manganese, are all inert on it at common temperatures. Zinc is dissolved by it, and hydrogen gas is disengaged by the decomposition of water, and there remains in solution hypo-sulphuric acid combined with oxide of zinc. It completely saturates salifiable bases, and affords neutral and soluble compounds with baryta, strontia, lime, and protoxide of lead; whereas sulphuric acid yields insoluble compounds with all those bases. At common temperatures these salts are permanent, but, when heated, sulphurous acid escapes, and they pass to the state of sulphates, which are still neutral.

609. Hypo-sulphuric acid has been inferred to be composed of 100 parts of sulphur + 135 oxygen, setting apart that which is in the water essential to its existence; or we may consider it as a compound of 100 parts of sulphurous acid + 125 of sulphuric. H. 400. Composition.

610. *Sulphuric Acid and Ammonia*—*Sulphate of Ammonia*—may be obtained by passing ammonia into sulphuric acid; but it is usually prepared by saturating dilute sulphuric acid with *carbonate of ammonia*, or by decomposing muriate of ammonia by sulphuric acid. It is the *secret sal-ammoniac* of some old writers. This salt is important as a source of the muriate of ammonia, (542) which is obtained by sublimation from a mixture of common salt and sulphate of ammonia; by this process sulphate of soda is also formed. Sulphate of ammonia.

Sulphate of ammonia dissolves in twice its weight of water at 60° or in an equal weight of boiling water, and consists of 1 proportional of sulphuric acid = 40 + 1 proportional of ammonia = 17 combined, according to Dr Thomson, with 1 atom, and according to Berzelius with 2 atoms of water. By crystallization it affords six-sided prisms. Its taste is bitter and pungent. When heated, it melts and in part sublimes, ammonia is given off, and a *super-sulphate* remains, consisting of 2 proportionals of acid + 1 of alkali. Composition

611. *Native Sulphate of Ammonia* is sometimes found in volcanic products; it occurs in stalactitic concretions of a whitish or yellowish colour, and covered with a white efflorescence.

612. *Sulphur and Chlorine*—*Chloride of Sulphur*.—This compound was first described by Dr Thomson, in 1804.* When sulphur is heated in chlorine, it absorbs rather more than twice its weight of that gas. 10 grains of sulphur absorb nearly 30 cubic inches of chlorine, and produce a greenish-yellow liquid, consisting of 16 sulphur + 36,0 chlorine, and represented, therefore, by the number 52. It exhales suffocating and irritating Chloride of sulphur.

* Nicholson's Journal, vol. vi.

fumes when exposed to the air. Its specific gravity is 1,6. It does not affect dry vegetable blues; but when water is present, it reddens them, but not till by its action on the water or on hydrogen, muriatic acid has been produced: sulphur is deposited, and sulphurous and sulphuric acids are formed. It dissolves sulphur and phosphorus.*

Sulphuretted
hydrogen.

613. *Sulphur and Hydrogen*—*Sulphuretted Hydrogen gas*—*Hydrothionic acid*.—This gaseous compound of sulphur and hydrogen was first investigated by Scheele in 1777. It may be obtained by presenting sulphur to nascent hydrogen, which is the case when sulphuret of iron is acted upon by dilute sulphuric acid.

Process for
obtaining.

The sulphuret of iron may be prepared in the following manner. A bar of iron is to be heated to a white or welding heat in a smith's forge, and, in this state, is to be rubbed with a roll of sulphur. The metal and sulphur unite, and form a liquid compound, which falls down in drops. These soon congeal; and the compound must be preserved in a well closed phial.† A portion of this may be introduced into a retort or gas bottle and diluted sulphuric acid poured upon it, as in the process for obtaining hydrogen gas (371).

It may also be conveniently obtained by heating bruised sulphuret of antimony in muriatic acid. To a mixture of powdered sulphuret of antimony (crude antimony of the shops) with 5 or 6 times its weight of muriatic acid (sp. gr. 1.160 or thereabouts) contained in a retort or gas bottle, apply the heat of a lamp. Sulphuretted hydrogen will be disengaged in great abundance.

Absorbed by
water.

614. Sulphuretted hydrogen gas may be collected over water, though, by agitation, that fluid absorbs nearly thrice its bulk; it should be received into bottles provided with glass stoppers, and after filling them entirely with the gas, the stopper should be introduced.

Liquefaction
of sulphuretted
hydrogen.

615. Mr Faraday obtained sulphuretted hydrogen in a liquid form by producing it under pressure. A tube being bent, and sealed at the shorter end, strong muriatic acid was poured in through a small funnel, so as nearly to fill the short leg without soiling the long one. A piece of platinum foil was then crumpled up and pushed in, and upon that were put fragments of sulphuret of iron, until the tube was nearly full. In this way action was prevented until the tube was sealed. If it once commences, it is almost impossible to close the tube in a manner sufficiently strong, because of the pressing out of the gas. When closed, the muriatic acid was made to run on to the sulphuret of iron, and then left for a day or two. At the end of that time, much protomuriate of iron had formed, and on plac-

* *Sulphur and Iodine* readily unite and form a black crystallizable compound, resembling sulphuret of antimony, first described by M. Gay-Lussac.—*Annales de Chimie*, 91.

† The sulphuret, prepared by melting iron filings with sulphur in a crucible, does not answer the purpose equally well, because the gas, which it affords, is mixed with a good deal of hydrogen gas.

ing the clean end of the tube in a mixture of ice and salt, warming the other end if necessary, by a little water, sulphuretted hydrogen in the liquid state distilled over.

616. The liquid sulphuretted hydrogen was colourless, limpid, and excessively fluid. It did not mix with the rest of the fluid in the tube, which was no doubt saturated, but remained standing on it. When a tube containing it was opened, the liquid immediately rushed into vapour; and this being done under water, and the vapour collected and examined, it proved to be sulphuretted hydrogen gas. As the temperature of a tube containing some of it rose from 0° to 45°, part of the fluid arose in vapour and its bulk diminished; but there was no other change: it did not seem more adhesive at 0° than at 45°. Its refractive power appeared to be rather greater than that of water: it decidedly surpassed that of sulphurous acid. The pressure of its vapour was nearly equal to 17 atmospheres at the temperature of 50° F. Its specific gravity appeared to be 0,9*

Properties.

617. When in the form of gas, the smell of sulphuretted hydrogen is extremely offensive, resembling that of putrefying eggs, or of the washings of a gun barrel, to which indeed it imparts their offensive odour. It exists in some mineral waters.

Properties:

618. The specific gravity of sulphuretted hydrogen has been variously stated. Sir H Davy states the weight of 100 cubic inches at 36,5 grains, and its specific gravity, therefore, at 1,196. Gay-Lussac and Thenard determined its specific gravity to be 1,1912 by experiment, or 1,1768 by calculation; and 100 cubic inches, according to the first of these two numbers, should weigh 36,33 grains.† The latest attempt to ascertain its specific gravity, is that of Dr Thomson, the result of which was 1,1788, or, more correctly he conceives, 1,1805. Hence 100 cubic inches (bar. 30, therm. 60°) would weigh 35,89 grains.

Specific gravity.

119. To determine its composition, we have only to subtract the specific gravity of hydrogen from that of the compound gas, and the remainder will show the weight of the sulphur. Thus

Composition.

| | |
|--|-------|
| Sp. grav. of sulphuretted hydrogen gas | 1,180 |
| — hydrogen gas | 0,069 |
| | <hr/> |
| | 1,111 |

It is constituted, therefore, of 1 volume of the vapour of sulphur=1 atom (1,111)+1 vol. of hydrogen gas=1 atom (0,069). But the numbers 0,069 and 1,111 are in the proportion very nearly of 1 to 16, which gives exactly the same relative weight for the ultimate particle of sulphur, as that deduced from the composition of sulphuric acid. H. 1. 446.

620. It is inflammable, and during its slow combustion, sulphur is deposited, and water and sulphurous acid formed. It extinguishes flame.

* *Phil. Trans.* 1823, p. 192.

† *Ann. de Chim.* 81. 26.

23

621. It appears to be one of the most unrespirable of all the gases, for a small bird died immediately in air containing $\frac{1}{1500}$ of its volume of sulphuretted hydrogen; a dog perished in air mingled with $\frac{1}{800}$ and a horse in air containing $\frac{1}{250}$. (Thenard, iii. 601).

Action on
metals.

622. It tarnishes silver, mercury, and other polished metals, and instantly blackens white paint and solution of acetate of lead. By direct experiments, Dr Henry has found that one measure of this gas, mixed with 20,000 measures of hydrogen, or of carburetted hydrogen, or common air, produces a sensible discoloration of white lead, or of oxide of bismuth, mixed with water, and spread upon a piece of card.

Hydro sul-
phuric acid of
Gay Lussac.

623. Water, saturated with this gas, reddens infusion of violets, in this respect producing the effect of an acid. From this and other properties, some of the German chemists have proposed for it the name of *hydrothionic acid*; and Gay-Lussac has given it the very objectionable name of *hydro-sulphuric acid*, a term which would be much more properly applied to liquid sulphuric acid.

Solution.

624. Sulphuretted hydrogen, both in the state of a gas and of watery solution, precipitates most metallic solutions, and is hence an exceedingly delicate test of the presence of most of the metals.

625. Water impregnated with sulphuretted hydrogen, when exposed to the atmosphere, becomes covered with a pellicle of sulphur. Sulphur is even deposited when the water is kept in well-closed bottles.

626. On the addition of a few drops of nitric or nitrous acid to the watery solution sulphur is instantly precipitated. In this case the oxygen of the acid combines with the hydrogen of the gas, and the sulphur is separated. The gas itself, also, is decomposed when transmitted through sulphuric, nitric, or arsenic acids.*

Inflamed by
nitric acid.

627. Berzelius has found that when a few drops of fuming nitric acid are put into a flask filled with sulphuretted hydrogen, the hydrogen is oxidized by the nitric acid, and the sulphur is disengaged in a solid form. If the flask be closed by the finger, so that the gas which becomes heated cannot escape, its temperature is raised so much as to produce combustion with a beautiful flame, and a slight detonation which forces the finger from the mouth of the flask. This experiment may be made with safety in a flask containing four or five cubical inches of gas.

Exp.

Results of its
detonation
with oxygen.

628. When one volume of sulphuretted hydrogen, and 1.5 of oxygen are inflamed in a detonating tube, 1 volume of sulphurous acid is produced, and water is formed. Sulphuretted hydrogen may also be decomposed by the Voltaic flame, in the apparatus shown at fig. 43, or by a succession of electric sparks. Its volume is unchanged, but the sulphur is thrown down.

Pl. ii.

629. Chlorine, bromine and iodine decompose sulphuretted hydrogen; sulphur is deposited, and muriatic, hydrobromic and hydriodic acids are formed. It is also decomposed by the metal potassium, which absorbs the sulphur and liberates pure hydrogen when heated in the gas.

Decomposed
by chlorine
bromine and
iodine.

630. When sulphuretted hydrogen is mixed with its volume of nitric oxide over mercury, a diminution of bulk ensues, in consequence of the production of water; sulphur is deposited and nitrous oxide remains in the vessel.

Decomposed
by nitric ox-
ide, &c.

631. When two volumes of sulphuretted hydrogen are mixed in an exhausted balloon with one of sulphurous acid, they mutually decompose each other, occasioning the production of water, and the deposition of sulphur; if the gases be perfectly dry, the action is slow.

632. It is decomposed, also, when long kept in a state of mixture with atmospheric air, the oxygen of which combines with the hydrogen, and forms water, while the sulphur is precipitated.

633. Sulphuretted hydrogen is copiously absorbed by alkalis, and by all the earths excepting alumina and zirconia. This property affords a ready method of ascertaining its purity, for if it be agitated with a solution of potassa, in the apparatus fig. 104 or 105, the unabsorbed residue will show the amount of the impurity, which is commonly hydrogen gas. Its alkaline and earthy combinations are termed *hydro-sulphurets*. H. 1. 444.

Absorbed by
alkalies and
earths.

Pl. v.

634. *Sulphuretted hydrogen and ammonia* readily unite in equal volumes, and produce *hydrosulphuret of ammonia*. At first white fumes appear, which become yellow, and a yellow crystallized compound results, consisting of 17 sulphuretted hydrogen + 17 ammonia. It is of much use as a test for the metals, and may be procured by distilling at nearly a red heat, a mixture of 6 parts of slacked lime, 2 of muriate of ammonia, and 1 of sulphur.

Hydrosulphu-
ret of ammo-
nia.

635. Fig. 108, represents the disposition of the apparatus for this process: *a*, a small furnace; *b*, a tubulated earthen retort containing the above materials; *c*, an adapting tube; *e*, a glass balloon for condensing the vapour; *f*, a receiver; *g*, a bottle of water, into which the glass tube, issuing from the upper part of the receiver, *e*, is made to dip about half an inch.

How obtain-
ed.

Pl. v.

The product in the bottle *f* may be mixed with the water in *g*, and the whole used for washing out the receiver *e*. In its concentrated state, this compound exhales white fumes, as was first remarked by Boyle, whence it was termed *Boyle's Fuming Liquor*, or *Volatile Liver of Sulphur*. It is a deep yellow liquid, smelling like a mixture of sulphuretted hydrogen and ammonia.

When kept in common white glass vessels it renders them brown or black, in consequence of its action on the oxide of lead which the glass contains.

Theory.

The hydro-sulphuric acid, which, according to Thenard, composes the liquor of Boyle, can only have been produced at the expense of the hydrogen of the muriatic acid of the sal-ammoniac. The muriatic acid and one portion of lime (oxide of calcium) are decomposed; the sulphur making a part of the mixture, unites in part to the hydrogen of the acid to form hydro-sulphuric acid, which combines with the ammonia; and in part to the oxygen of the oxide of calcium, to give rise to the sulphurous or sulphuric acid; the chlorine and calcium unite and constitute the larger part of the residuum: while another portion of the sulphur combines with the lime that is not decomposed and transforms it into sulphuret of lime.

The smoking takes place in oxygen gas or atmospheric air, but not in nitrogen or hydrogen; the effect probably depending, therefore, on the combination of oxygen with the hydrogen of the liquor, causing a deposition of sulphur. Th. ii. 662.

Super-sulphuretted hydrogen.

636. *Super-Sulphuretted Hydrogen*.—This compound was discovered by Scheele, and afterwards examined by Berthollet.* It is obtained when hydro-sulphuret of potassa (formed by boiling the flowers of sulphur with liquid potassa) is poured, by little and little, into muriatic acid. A very small portion only of gas escapes; and while the greater part of the sulphur separates, one portion of it combines with the sulphuretted hydrogen; assumes the appearance of an oil; and is deposited at the bottom of the vessel. Or, dissolve sulphur in a boiling solution of pure potassa; and into a phial containing about $\frac{1}{3}$ of its capacity of muriatic acid, of the specific gravity 1.07, pour about an equal bulk of the liquid compound. Cork the phial, and shake it; the hydroguretted sulphur, gradually settles to the bottom in the form of a brown, viscid, semifluid mass. Its properties are the following:

Properties.

637. Its taste and smell resemble those of putrid eggs, but are less offensive. Its precise specific gravity is unknown, but it is heavier than water, and descends through it. It is inflammable and burns in the air with a smell of sulphurous acid.

If gently heated, sulphuretted hydrogen gas exhales from it; the bi-sulphuret loses its fluidity; and a residue is left, consisting merely of sulphur.

It combines with alkalies and earths; and forms with them a class of substances called *hydroguretted sulphurets*.

Composition.

638. It is constituted according to Mr Dalton, of two atoms of sulphur = 32, with one atom of hydrogen, and is represented by the number 33. It consists per cent. of

| | |
|--------------------|-------|
| Sulphur | 96.75 |
| Hydrogen | 3.25 |
| | <hr/> |
| | 100. |

639. There are, therefore, three distinct combinations of sulphur and its compounds with alkalies and earths. The first

consist, simply, of sulphur, united with a base, and are properly called *sulphurets*. The second are composed of sulphuretted hydrogen, united with a base, and are called *hydro-sulphurets*. The third contain bi-sulphuretted hydrogen, attached to a base, and constitute *hydroguretted sulphurets*.

640. The hydroguretted sulphurets may be also formed by boiling along with a sufficient quantity of water, the alkaline or earthy base, with flowers of sulphur. Or by digesting, in a gentle heat, a hydro-sulphuret with powdered sulphur, an additional portion of which is thus dissolved, while part of the sulphuretted hydrogen escapes.

641. Hydroguretted sulphurets have a deep greenish yellow colour; an acrid, bitter taste; and excessively offensive smell. They deposite sulphur when kept in close vessels; become more transparent and lighter coloured; and less offensive to the smell. They rapidly absorb oxygen from the atmosphere, and are hence employed in eudiometry.

They are decomposed by dilute sulphuric, muriatic and certain other acids, sulphuretted hydrogen gas is evolved, and sulphur precipitated. H. 1. 447.*

SECTION IV. *Phosphorus.*

642. Phosphorus was discovered about the year 1669, by Brandt, an alchemist of Hamburg, while employed in the research after the art of converting the baser metals into gold and silver; and afterwards by Kunckel, a German chemist. It was originally prepared from urine; but Scheele afterwards described a method of obtaining it from bones. In 1769 Gahn, of Sweden, having discovered the phosphoric acid in bones, invented the method of preparing phosphorus which is now generally followed.

Time of discovery.

643. The object of the process is to bring phosphoric acid in contact with charcoal at a strong red heat. The charcoal takes oxygen from the phosphoric acid; carbonic acid is disengaged, and phosphorus is set free.

Method of preparing.

When bones are employed they should first be ignited in an open fire till they become quite white, so as to destroy all the animal matter they contain, and oxidize the carbon proceeding from its decomposition. The calcined bones, of which phosphate of lime constitutes nearly four fifths, should be reduced to fine powder, and be digested for a day or two with half their weight of concentrated sulphuric acid, so much water being added to the mixture as to give it the consistence of a thin paste. The phosphate of lime is decomposed by the sul-

* Sulphur and Nitrogen do not form any definite compound, though the nitrogen evolved during the decomposition of certain animal substances, often seems to contain sulphur.

phuric acid, and two new salts are generated, the insoluble sulphate, and the soluble bi-phosphate of lime. On the addition of boiling water the bi-phosphate is dissolved, and may be separated by filtration from the sulphate of lime. The solution is then evaporated to the thickness of syrup and mixed with one fourth of its weight of charcoal in powder. This mixture is put into the coated earthen retort, fig. 109 *a*, placed in a small portable furnace *b*; the tube of the retort should be immersed about half an inch into the basin of water *c*. A great quantity of gas escapes, some of which is spontaneously inflammable, and when the retort has obtained a bright red heat, a substance looking like wax, of a reddish colour passes over: this, which is impure phosphorus may be rendered pure by melting it under warm water, and squeezing it through a piece of fine shamois leather: but great care must be taken that none adheres to the nails or fingers, which would inflame on taking them out of the water, and produce a painful and troublesome burn. It is usually formed into sticks, by pouring it, when fluid, into a funnel tube under water.

Pl. v.

Another process.

Phosphorus may also be procured by adding to urine a solution of lead in nitric acid, which precipitates a phosphate of lead. This, when well washed, dried, and distilled in a stone-ware retort, yields phosphorus. Or a solution of phosphate of soda (which may be bought at the druggists), mixed with one of acetate of lead, in the proportion of one part of the former salt to $1\frac{1}{4}$ of the latter, yields a precipitate of phosphate of lead, from which phosphorus may be procured by distillation with charcoal, but at considerable more expense. H. 1. 377.*

Properties.

644. Phosphorus has generally a flesh-red colour, but when carefully purified, may be obtained colourless, and transparent. Its specific gravity is 1.77. In consequence of its inflammability it must be kept under water in well closed bottles. It is so soft that it readily yields to the knife.

Fusing point.

It melts at about 109° or 110° F. and boils at 500° . When melted it must be covered with water, in order to prevent it from inflaming. Exposed to a heat of between 140° and 160° F., and suddenly cooled, it becomes black; but if slowly congealed, it remains transparent and colourless; when cooled at a moderate rate, it assumes the semi-transparency of horn.† By the fusion and careful refrigeration of a large quantity of phosphorus M. Frantween has obtained fine crystals of an octoedral form;‡ and M. Bellani has found that it remains fluid, even many days, when in tranquillity, at the temperature of 54° F.

May be crystallized.

* In performing this distillation, a high temperature is required, so that the furnace should be sufficiently capacious to hold a body of charcoal piled up above the retort, which, as earthen ware becomes permeable to the vapour of phosphorus at a red heat, must be coated with a mixture of slaked lime and solution of borax; this mixture may be laid on with a brush, in two or three successive coats, and forms an excellent *vitriifiable lute*.

† According to Thenard, it is not all phosphorus that exhibits these properties, but only that which has undergone repeated distillations.—*Traité de Chim.* 1. 212.

‡ *Quart. Jour N. S.* iii. 206.

and may be even cooled down to 37° : but as soon as it has acquired the lowest temperature which it can bear without solidifying, the moment it is touched with a body at the same temperature, it solidifies so quickly that the touching body cannot penetrate its mass.*

At 550° it boils, air being excluded, and rapidly evaporates. When exposed to air, it exhales luminous fumes, having a peculiar alliaceous odour; it is tasteless and insoluble in water, but proves poisonous when taken into the stomach.†

645. If a cylinder of phosphorus be introduced into a vessel of oxygen gas, over mercury, at a temperature not exceeding 80° F., no perceptible absorption will happen in 24 hours; but if, the temperature remaining the same, the pressure be diminished to $\frac{1}{10}$ th or $\frac{1}{100}$ th that of the atmosphere, the phosphorus will be surrounded by white vapours, will become luminous in the dark, and will absorb oxygen. Under ordinary pressures, a higher temperature is required to produce this effect; but it is remarkable, that if the density of the oxygen be reduced in the above proportion, by mixing it with azote, hydrogen, or carbonic acid, the phosphorus becomes luminous. Hence phosphorus absorbs oxygen from atmospheric air with an extrication of light. H. 1. 368. Exp.
Absorbs oxygen.

646. Phosphorus is inflamed by the application of a very gentle heat. According to Dr Higgins, a temperature of 60° is sufficient to set it on fire, when properly dry. It burns when heated to about 148° , (100° Brande) with a very brilliant light, or a white smoke, and a suffocating smell, and may even be inflamed in an atmosphere rarefied sixty times. (*Van Marum.*)

It may be set on fire by friction. Rub a very small bit between two pieces of brown paper; the phosphorus will inflame, and will set the paper on fire also. Exp.

In oxygen gas it burns with a very beautiful light; (292) and also in nitrous oxide, and chlorine gases. The product of the rapid combustion of phosphorus in oxygen gas is exclusively phosphoric acid. Every 100 parts, according to Lavoisier, gain an addition of 154; according to Davy 100 grains of phosphorus condense 135 grains of oxygen gas. It is probable that the true proportions are 100 of phosphorus to $133\frac{1}{3}$ oxygen, and that the atomic weight of phosphorus is 12. H. 1. 371. Exp.

In pure nitrogen, phosphorus is not the least luminous at any temperature.

647. If, instead of burning phosphorus with free access of air, it is heated in a confined portion of very rare air, it enters into less perfect combustion, and three compounds of phosphorus with oxygen are the result, each characterized by distinct properties. The first is a red solid, less fusible than phosphorus; the second is a white substance, more volatile than phosphorus; and the third, a white and more fixed body. The first appears Products of its imperfect combustion.

* *Quart. Jour.* N. S. iv. 469.

† *Orfila, Traité de Poisons*, II. P. ii. p. 186.

to be a mixture of unburned phosphorus, and phosphorous acid; the second to be phosphorous acid; and the third to be phosphoric acid.

Solution in
oil, &c.

648. Phosphorus is soluble in oils, and communicates to them the property of appearing luminous in the dark;* alcohol and ether also dissolve it, but more sparingly.

Exp.

This may be shown by pouring a small quantity of either of these liquids, in which phosphorus has been dissolved, upon the surface of warm water in a dark room.

Nature of
phosphorus.

649. The only information, which we possess, respecting the nature of phosphorus, is derived from the electro-chemical researches of Sir H. Davy. When acted upon by a battery of 500 pairs of plates in the same manner as sulphur, gas was produced in considerable quantities, and the phosphorus became of a deep red-brown colour. The gas proved to be phosphuretted hydrogen, and was equal in bulk to about four times the phosphorus employed. Hence hydrogen may possibly be one of its components; but no confirmation of the truth of this view is derived from the recent experiments of the same philosopher, which, indeed, are rather contradictory to it. H. 1. 370.

650. *Phosphorus and Oxygen*.—Phosphorus kept under water in a bottle partly filled with that fluid, and into which fresh air is occasionally admitted, becomes covered with a white insoluble crust. This has been by some regarded as an oxide of phosphorus. The red coloured matter which remains after the combustion of phosphorus, is also supposed to be an oxide. This substance is very inflammable and is used in the *phosphoric match boxes*. To prepare it for this purpose, a piece of phosphorus may be put into a small phial and melted and stirred about with a hot iron wire so as to coat its interior. A small quantity taken out upon the end of a brimstone match inflames upon coming in contact with the air. There are three *acid* compounds of phosphorus and oxygen, which have been termed *phosphorous*, *phosphoric*, and *hypophosphorous* acids.

Phosphorous
acid.

Process.

651. *Phosphorous Acid*.—Phosphorous acid cannot, according to Sir H. Davy, be obtained pure by exposing cylinders of phosphorus to atmospheric air; for when thus prepared, it always contains phosphoric acid. It can only be obtained in a state of purity, first by subliming phosphorus through corrosive sublimate; then mixing the product with water and heating it, till it becomes of the consistence of syrup. The liquid obtained is composed of pure phosphorous acid and water, which becomes solid and crystalline on cooling. It is acid to the taste, reddens vegetable blues, and unites with alkalies forming salts which are termed *Phosphites*.

Theory.

652. The theory of this process is, that when the compound of phosphorus and chlorine, formed in the first operation, is brought into contact with water, the water is decomposed; its

* M. Walcker has remarked that the luminous power is instantly destroyed by the addition of small quantities only of certain other substances, as the essential oils.—*Ann. der Phys.* 1826. 125.

hydrogen uniting with chlorine composes muriatic acid; and its oxygen combining with phosphorus forms phosphorous acid. From this mixture of acids, heat expels the muriatic.

653. The phosphorous acid exhales a disagreeable fetid odour; and yields, when strongly heated, penetrating white vapours. When heated in a glass ball, blown at the end of a small tube, a gas issues from the orifice of the tube, which inflames on coming into contact with the atmosphere. Hence it appears to contain an excess of phosphorus. The residuum in the ball is phosphoric acid. From the experiments of Rose on the phosphoric acid, Gay-Lussac infers that phosphorous acid must consist of

| | | | | | | |
|------------|-------|-------|-------|-----|-------|-----|
| Phosphorus | . . . | 56,81 | . . . | 100 | . . . | 132 |
| Oxygen | . . . | 43,19 | . . . | 76 | . . . | 100 |
| <hr/> | | | | | | |
| 100 | | | | | | |

These proportions do not differ materially from those stated by Dulong, who makes phosphorous acid to consist of 100 phosphorus + 74,88 oxygen.* They agree, also, still more nearly, with the statement of Berzelius, according to whom this acid consists of

| | | | | |
|------------|-------|--------|-----------|-------|
| Phosphorus | . . . | 56,524 | | 100, |
| Oxygen | . . . | 43,476 | | 76,92 |
| <hr/> | | | | |
| 100 | | | | |

Sir H. Davy, however, after a careful investigation of the constitution of phosphorous acid, has more lately been led to conclude that the oxygen, which it contains, is just one half of that existing in phosphoric acid; or that, in the former, 100 grains of phosphorus are united with only 67,5 of oxygen. Hence 100 grains of phosphorous acid must consist of

| | | |
|------------|-----------|------|
| Phosphorus | | 59,7 |
| Oxygen | | 40,3 |
| <hr/> | | |
| 100. | | |

And phosphorous acid, being probably constituted of 1 atom oxygen, + 1 atom of phosphorus, the weight of the latter atom may be inferred to be 11,62, or in round numbers 12. Phosphorous acid, then will be represented by 12 + 8 = 20. H. 1. 373.

654. *Phosphoric Acid* may be formed by burning phosphorus in excess of oxygen. There is intense heat and light produced, and white deliquescent flocculi line the interior of the receiver. It is produced in the same way by burning phosphorus under a dry bell-glass in atmospheric air. Phosphoric acid may be conveniently formed by the action of nitric acid on phosphorus. The phosphorus takes oxygen from the nitric acid, and a large quantity of the deutoxide of nitrogen is disengaged; but as the reaction is apt to be very violent, the process ought to be conducted with caution. It is best done by adding fragments of

Phosphoric acid.

How obtained.

* Phil. Mag. xlviii. 273.

phosphorus to concentrated nitric acid contained in a platinum capsule. A gentle heat is applied so as to commence, and, when necessary, to maintain a moderate effervescence; and when one portion of phosphorus disappears, another is added, till the whole of the nitric acid is exhausted. The solution is then evaporated to dryness.

A more economical method.

655. Phosphoric acid may be prepared most economically from bones.

On 20 pounds of calcined bone, finely powdered, pour 20 quarts of boiling water, and add $16\frac{1}{2}$ * pounds of sulphuric acid, diluted with an equal weight of water. Let these materials be well stirred together, and be kept in mixture about 24 hours. Let the whole be then put into a conical bag of linen to separate the clear liquor, and wash the residuum till the water ceases to taste acid. Evaporate the strained liquor in earthen vessels in a sand bath, and when reduced to about half its bulk, let it cool. A white sediment will form which must be allowed to subside; the clear solution must be decanted, and boiled to dryness in a glass vessel. A white mass will remain which may be fused in a crucible, and poured out into a clean copper dish. A transparent glass is obtained, which is the phosphoric acid in a glacial state; not, however, perfectly pure, but containing sulphate and phosphate of lime. According to Fourcroy and Vanquelin, it is, in fact, a super phosphate of lime, containing, in 100 parts, only 30 of uncombined phosphoric acid, and 70 of neutral phosphate of lime; but when prepared with the full proportion of sulphuric acid, Mr Dalton finds only 8 to 12 per cent. of the calcareous phosphate. H. To separate the latter, the acid liquor obtained by the action of sulphuric acid on bones, may be boiled for a few minutes with excess of carbonate of ammonia. The lime is thus precipitated as a carbonate, and the solution contains phosphate, together with a little sulphate of ammonia. The liquid after filtration, is evaporated to dryness, and then ignited in a platinum crucible, by which the ammonia and sulphuric acid are expelled.†

Properties.

656. Phosphoric acid is a deliquescent substance, and when in the flocculent state, as obtained by burning phosphorus under a dry bell-glass, it dissolves in water with a hissing noise and excites great heat when a small particle is put upon the tongue; when fused it has been called *glacial phosphoric acid*. It is inodorous, very sour, volatile at a bright red heat, but unchanged by it. As commonly prepared, it is an unctuous fluid. Specific gravity = 2.

Composition.

657. The composition of these acids of phosphorus has been investigated by Sir H. Davy, Dr Thomson, Berzelius, and Dulong. The subject is one of much difficulty, and the results of the two former chemists differ widely from those of the two latter. Dr Thomson infers from experiments made by Sir H. Davy and himself;‡ that phosphoric acid is composed of

| | | |
|----------------------|--------------|----------|
| Phosphorus | 12 | 1 atom. |
| Oxygen | 16 | 2 atoms. |

28

Hypo-phosphorous acid.

658. *Hypo-phosphorous Acid* was discovered by M. Dulong.§ It is prepared as follows: Upon 1 part of *phosphuret of barium* pour 4 parts of water, and when the evolution of phos-

* These are the proportions recommended by Pelletier and Dalton. A much less quantity of sulphuric acid is generally prescribed.

† For more minute directions see Henry, vol. 1. p. 375 edit. 10.

‡ *First Principles*.

§ *Annales de Chimie et Physique*, vol. ii. p. 141.

phuretted hydrogen gas has ceased, pour the whole upon a filter. To the filtered liquid add sulphuric acid as long as any precipitate forms; separate the precipitate, which is a compound of sulphuric acid and baryta, and the clear liquor now contains the hypo-phosphorous acid in solution.

When concentrated by evaporation, a sour viscid liquid is obtained, incapable of crystallization, and eagerly attractive of oxygen.

659. The compounds of this new acid with alkaline and earthy bases, are remarkable for their extreme solubility. Those of baryta, and strontia crystallize with great difficulty. The *hypo-phosphites* of potassa, soda, and ammonia, are soluble, in all proportions, in highly rectified alcohol. That of potassa is even more deliquescent than muriate of lime. They absorb oxygen slowly from the air, and when heated in a retort give the same products as the acid itself.

Union with bases.

In order to ascertain the properties of the elements of this acid, *Dulong*, its discoverer, converted a known quantity of it into phosphoric acid by means of chlorine, whence he infers it to consist of

Composition.

| | | | |
|--------------------|-------|---------|-------|
| Phosphorus | 72,75 | | 100, |
| Oxygen | 27,25 | | 37,44 |
| <hr/> | | | |
| 100, | | | |

These results are calculated on the supposition that hypo-phosphorous or per-phosphorous acid is a binary compound of oxygen and phosphorus; but it is doubtful whether it may not be a triple compound of oxygen, phosphorus, and hydrogen, or a *hydracid*; in which case its proper appellation would be *hydro-phosphorous acid*.

660. In his able investigation of the compounds of phosphorus, Sir H. Davy admits the existence of the new acid of *Dulong*, but deduces different proportions of its elements. The oxygen of this acid he infers to be the precise half of that which exists in phosphorous acid; or that 100 of phosphorus are united with 33,750 oxygen. But it has been already shown to be probable that phosphorous acid is composed of an atom of each of its elements; and it may, therefore, be inferred that hypo-phosphorous acid is constituted of one atom of oxygen weighing 8, and two atoms of phosphorus weighing $12 \times 2 = 24$, and the weight of the compound atom may be represented by 32. H. 1. 374.

661. *Phosphate of Ammonia* is a common ingredient in the urine of carnivorous animals. It may be obtained pure by saturating phosphoric acid with ammonia; it forms permanent octoëdral crystals soluble in two parts of water at 68°, of a bitterish saline taste, and specific gravity 1,8051. T.

Phosphate of ammonia.

| | |
|--------------------------|------------|
| It consists of | 28 acid |
| | 17 ammonia |
| <hr/> | |
| | 45 |

A source of
phosphoric
acid.

This salt is the best source of pure phosphoric acid, for if it be exposed to a red heat in a platinum vessel, the ammonia evaporates, and the acid is obtained in the form of a transparent glass, very deliquescent and pure. The phosphate of ammonia for this purpose may be conveniently and economically prepared by saturating the impure acid obtained from bones (655) with carbonate of ammonia, filtering and evaporating to dryness.

Union with
chlorine.

662. *Phosphorus and Chlorine*.—These elements unite in two proportions forming two definite compounds, the *protochloride*, and *perchloride* of phosphorus.

Perchloride.

663. When phosphorus is submitted to the action of chlorine, it burns with a pale yellow flame, and produces a white volatile compound which attaches itself to the interior of the vessel, and which is the *perchloride of phosphorus*. This substance was long mistaken for phosphoric acid, but its easy volatility is alone sufficient distinction; it rises in vapour at 200° . It is fusible and crystallizable: and acts violently on water, the hydrogen of which forms, with the chlorine, muriatic acid; while the oxygen with the phosphorus forms phosphoric acid. When passed through a red-hot porcelain tube with oxygen, phosphoric acid is produced and chlorine evolved, which shows that oxygen has a stronger attraction for phosphorus than chlorine.

When phosphorus is burned in chlorine, one grain absorbs 8 cubic inches; so that the compound formed must be regarded as containing 1 proportional of phosphorus, and 2 of chlorine, or 12 of phosphorus + 72 of chlorine, and its number is 84.

664. With ammonia perchloride of phosphorus forms a singular compound, which though consisting of three volatile bodies, remains unchanged at a white heat, and is insoluble in water.

Chloride of
phosphorus

665 *Chloride or Protochloride of Phosphorus*, consisting of 12 phosphorus + 36 chlorine, is procured by distilling a mixture of phosphorus and *corrosive sublimate*, which is a perchloride of mercury. In this experiment *calomel*, or protochloride of mercury, is formed, and the phosphorus combines with one proportional of chlorine.

Properties.

666. The chloride of phosphorus, when first obtained, is a liquid of a reddish colour: but it soon deposits a portion of phosphorus, and becomes limpid and colourless. Its specific gravity is 1.45. Exposed to the air it exhales acid fumes: it does not change the colour of dry vegetable blues. Chlorine converts it into perchloride. Ammonia separates phosphorus, and produces the singular triple compound as before adverted to (664.)

Action upon
water.

667. Chloride of phosphorus acts upon water with great energy, and produces muriatic and *phosphorous* acids, while the perchloride produces muriatic and *phosphoric* acids: for, as in the perchloride there are two proportionals of chlorine, so in acting upon water, two of oxygen must be evolved, which

uniting to one of phosphorus generate phosphoric acid. The chloride of phosphorus on the contrary, containing one proportional of chlorine, produces muriatic acid and phosphorous acid, when it decomposes water, as the following tables show :

| | | Chloride of Phosp. | | Water. |
|----------------------------|--|-----------------------|---------------------------------|----------------------|
| Before de- composition. | { 1 Chlorine = 36 1 Phospho. = 12 } | 48. | 1 Hydrog. = 1 1 Oxygen = 8. | } 9. |
| | | Muriatic Acid. | | Phosphorous Acid. |
| After de- composition. | { 1 Chlorine = 36 1 Hydrog. = 1 } | 37. | 1 Phospho. = 12 1 Oxygen = 8 | } 20 |

But the phosphorous acid, thus produced, always contains water, which it throws off when heated in ammonia, forming, with that alkali, a dry phosphite. This experiment shows that the *hydrophosphorous acid* consists of 2 proportionals of phosphorous acid = 40 + 1 water = 9, its number is therefore, 49.

668. *Phosphorus and Bromine*.—According to M. Balard phosphorus and bromine made to act on each other in an atmosphere of carbonic acid gas form two compounds, one, which is solid, sublimes and crystallizes on the upper part of the vessel, a fluid substance remaining beneath and appearing to contain less bromine than the former. It remained fluid at 10° F. and was readily volatile forming pungent vapours. It dissolved excess of phosphorus, acted powerfully on water, producing much gaseous hydro-bromic acid.

Phosphorus
and Bromine.

The deuto-bromide of phosphorus is a yellow solid, readily made by adding bromine to the previous compounds; easily fusible and vaporizable: by refrigeration both the vapours and fluid crystallized. By contact with the air it fumed, the water in it being decomposed, and producing hydro-bromic and phosphoric acids. Chlorine decomposed these compounds, producing bromine and chloride of phosphorus.*

669. *Iodide of Phosphorus*.—Iodine and phosphorus combine readily in the cold, evolving so much caloric as to kindle the phosphorus, if the experiment is made in the open air; but in close vessels no light appears. The combination takes place in several proportions which have not yet been determined. Its most interesting property is that of decomposing water with formation of hydriodic and phosphoric acids.

Iodide.

670. *Phosphorus and Hydrogen*.—*Phosphuretted Hydrogen*.—*Hydroguret of Phosphorus*.—When phosphorus is presented to nascent hydrogen, two gaseous compounds result. The one inflames spontaneously upon the contact of the atmosphere. This may be procured by boiling phosphorus in a solution of caustic potassa; or better, by acting upon *phosphu- ret of lime* by dilute muriatic acid.†

Union with
hydrogen.

* *Quart. Jour.* 44, 390.

† M. Viala finds that when phosphorus is introduced into a receiver containing a weak solution of an alkali, phosphuretted hydrogen is formed, and evolved in a few hours without the application of heat.—*Jour. de Pharm.* Feb. 1827.

Method of obtaining phosphuretted hydrogen

671. In preparing this gas from phosphorus and solution of potassa, for exhibiting its spontaneous accension, both the body and neck of the retort should be entirely filled with the solution; a retort holding from half a pint to a pint may be employed.* Soon after the solution boils, the gas is evolved in abundance, and inflames on escaping into the air.

Thomson's method.

672. For obtaining this gas by the second process, Dr Thomson gives the following directions: Fill a small retort with water acidulated by muriatic acid, and then throw into it a quantity of phosphuret of lime in lumps. Plunge the beak of the retort under water, and place over it an inverted jar filled with that liquid. Phosphuretted hydrogen gas is extricated in considerable quantity, and soon fills the glass jar. Half an ounce of phosphuret of lime yields about 70 cubic inches of this gas.†

Properties.

673. This gas is colourless, has a nauseous odour like onions, a very bitter taste and inflames when mixed with air, a property which it loses by being kept over water; water takes up two *per cent.* of the gas, and acquires a bitter taste, and the smell of onions.

Exp.

674. When bubbles of phosphuretted hydrogen are let up into a jar of oxygen, they burn with greatly increased splendour; in chlorine too they burn with a beautiful pale blue light, forming muriatic acid and perchloride of phosphorus. In a narrow tube it may be mixed with oxygen without exploding, in which case it is deprived of its phosphorus without suffering any change of bulk. It burns when thrown up into nitrous oxide.

Composition.

675. For our knowledge of the composition of this gas, we are chiefly indebted to Dr Thomson, who has shown that the hydrogen suffers no change of bulk in uniting to the phosphorus; so that the difference of weight between this gas and pure hydrogen, indicates the weight of phosphorus. It may be regarded as containing one proportional of phosphorus and one of hydrogen, or $12 + 1 = 13$. Its specific gravity is very variable. Sir H. Davy has obtained it, from phosphorus and alkaline lixivia, of all specific gravities, from ,400 to ,700; Mr Dalton states it at ,850, air being 1,000, and Dr Thomson at ,9027. The quantity absorbed by water is fixed by Davy

* As the gas would explode should much atmospheric air remain in the retort, it will be best to introduce an atmosphere of hydrogen, which may be done as follows. After introducing both the phosphorus and the solution fix the neck of the retort on an inclined plane formed of a block of wood, fig. 110, the retort being held in an upright position its neck may be passed through the rings attached to the block; placing the finger over the beak of the retort carefully invert it under the surface of water contained in a small bowl. The solution should now be displaced from the neck of the retort and about one third of its body, by passing up *hydrogen* gas from a gas bottle or flask having a bent tube—or the retort being held in a vertical position by an assistant, the beak being kept under the surface of the water in the bowl, the gas may be passed up in the usual manner. It will be found necessary after all the solution has been expelled from the neck, to incline the body of the retort so as to allow a part of what remains in the body to flow into it, which is to be expelled as at first.

† Thomson's *System*, vol. i. 272.

at $\frac{1}{6}$ its bulk, and by Dalton at $\frac{1}{27}$, Dr Thomson makes it $\frac{1}{36}$. H. 1. 439.

676. When phosphuretted hydrogen is mixed with oxygen, it requires a volume and a half of the latter gas for its perfect combustion; and as the hydrogen would require half its volume of oxygen for the production of water, the remaining volume must unite to the phosphorus to produce phosphoric acid.

677. *Bihydroguret of phosphorus*.—*Hydrophosphoric Gas*. Hydrophosphoric gas.
—The next compound of phosphorus and hydrogen has been called, by Sir H. Davy, *hydrophosphoric gas*. It is procured by heating the solid hydrophosphorous acid in a very small retort. The gas must be collected over mercury, for water absorbs one-eighth its volume. Its specific gravity to hydrogen is as 12 to 1*. It is not spontaneously inflammable, but explodes when heated with oxygen. It inflames spontaneously in chlorine, one volume requiring four of chlorine for its perfect combustion. Its smell is less disagreeable than the former. It con-

sists of 2 of hydrogen and 1 of phosphorus $2 + 12 = 14$; but the two volumes of hydrogen are condensed into one; consequently when the gas is decomposed, as for instance, by subliming sulphur in it, two volumes of sulphuretted hydrogen are formed.

678. The existence of different varieties of phosphuretted hydrogen has been denied by Mr Dalton, whose experiments have led him to the conclusion, that the apparent diversities of composition are occasioned by the admixture of various proportions of free hydrogen, and phosphuretted hydrogen. H.†

679. *Phosphorus and Sulphur* are capable of combining. Union with sulphur.
They may be united by melting them together in a tube exhausted of air, or under water. In this last case they must be used in small quantities; at the moment of their action, water is decomposed, sometimes with explosions. They unite in many proportions. The most fusible compound is that of one and a half of sulphur to two of phosphorus. This remains liquid at 40° F. When solid, its colour is yellowish-white. It is more combustible than phosphorus, and distils undecomposed at a strong heat. U. 638.‡

SECTION V. Carbon.

680. The purest form of this elementary substance is the diamond. Diamond.

681. The diamond, which Sir I. Newton had sagaciously inferred to be a combustible body, from its powers of refracting

* Davy.

† Phosphorus and Nitrogen produce no definite compound, though in some cases of animal decomposition the evolved nitrogen appears to hold phosphorus in solution.

‡ See, also, Faraday, *Jour. Roy. Instit.* iv. 361.

light, was first shown by Guyton* to contain carbon, and his experiments led him to conclude that the diamond is the only form of pure carbon; and that charcoal is a compound of carbon and oxygen, or an oxide of carbon. The experiments of Messrs Allen and Pepys have, however, gone far towards proving that the diamond and charcoal, though so widely remote from each other in external characters, are, as to their chemical nature, identically the same; and that the difference between them, in all probability, results merely from the respective states of aggregation of their particles. H. 1. 335.

Charcoal,

682. Another form of carbon is *charcoal*, the purest variety of which is *lamp-black*.

method of
preparing.

Charcoal may be prepared by heating pieces of wood, covered with sand to redness, and keeping them in that state for about an hour. They are converted into a black brittle substance, which appears to be the same from whatever kind of wood it has been procured.

Common charcoal employed as fuel is usually made of oak, chesnut, elm, beech, or ash wood, the white and resinous woods being seldom used. Young wood affords a better charcoal than large timber, which is also too valuable to be thus employed. It is formed into a conical pile, which being covered with earth, or clay; is suffered to burn with a limited access of atmospheric air, by which its complete combustion, or reduction to ashes, is prevented.

Another, and a more perfect mode of preparing charcoal, consists in submitting it to a red heat in a kind of distillatory apparatus consisting of cast iron cylinders, from which issue one or more tubes for the escape of gaseous matters. The makers of gunpowder particularly prefer this process †

Lamp-black.

683. Lamp-black is prepared principally by turpentine manufacturers from refuse and residuary resin, which is burned in a furnace, so constructed, that the dense smoke arising from it may pass into chambers hung with sacking, where the soot is deposited, and from time to time swept off, and sold without any further preparation.‡ When lamp-black has been heated red hot in a close vessel, it may be considered as very pure carbon. A very pure charcoal is obtained from spirit of wine.

684 The quantity of charcoal obtained from different kinds of wood is liable to much variation. See *Tables*.

Its properties.

685. Charcoal is a black, insoluble, inodorous, insipid, brittle substance; an excellent conductor of electricity, but a bad conductor of heat; unchanged by the combined action of air and moisture at common temperatures; and easily combustible in oxygen gas.

Effect of Gal-
vanism.

686. Professor Silliman first observed, on subjecting cylindrical pieces of charcoal, tapered to a point, to the galvanic

* *Ann. de Chimie*, xxxi.

† See *Pyroligneous Acid*.

‡ *Aikin's Dictionary*. Art. *Charcoal*.

deflagrator of Dr Hare, (254) when in powerful action, that the charcoal point of the positive pole instantly shot out $\frac{1}{10}$ th, $\frac{1}{8}$ th, or even $\frac{1}{4}$ of an inch. The charcoal of the negative pole underwent, in the mean time a change precisely the reverse, its point disappearing, and a crater-shaped cavity being substituted in its stead. By placing a piece of metal at the negative pole in lieu of charcoal; it was ascertained by the absence of the usual phenomena, that the increase, before observed in the charcoal at the positive pole, was occasioned by an actual transference of charcoal, from the former to the latter. This appearance is attributed by Prof. Silliman to the fusion of the charcoal; but by others to impurities present in it *

687. Charcoal is capable of destroying the smell and taste of a variety of vegetable and animal substances.† The use of charring piles; of throwing charcoal into putrid water; of wrapping it in clothes that have acquired a bad smell; of adding it to port wine, with a view of making it tawny; depends upon the above properties. Uses of charcoal.

688. The charcoal of wood, besides its use as a fuel, is necessary to the preparation of that kind of iron which is used for wire; to the cementation of steel; and to the preparation of gun-powder. The charcoal prepared from pit-coal, called coke, Coke. is less pure, and, besides other substances, generally contains sulphur, but it has the advantage of being heavier and more compact, in consequence of which it is better adapted for burning in furnaces in which there is a powerful blast of air. H. 1. 330.

689. Newly-made charcoal has the property of absorbing certain quantities of the different gases. In the experiments of M. Theodore de Saussure,‡ the charcoal was heated red hot, then suffered to cool under mercury, and introduced into the gas. The following are the volumes of different gases absorbed by a volume of charcoal = 1. Absorbs gases,

| | | | |
|---------------------------------|----|--------------------------|------|
| Ammonia | 90 | Olefiant gas | 35 |
| Muriatic acid | 85 | Carbonic oxide | 9,42 |
| Sulphurous acid | 65 | Oxygen | 9,25 |
| Sulphuretted hydrogen | 55 | Nitrogen | 7,5 |
| Nitrous oxide | 40 | Hydrogen | 1,75 |
| Carbonic acid | 35 | | |

The absorption was always at its maximum at the end of 24 hours.

690. The results of these experiments are widely different from those of Count Morozzo.§ It would also appear, that this property depends upon the mechanical texture of the charcoal, and consequently will vary in the different woods; for by exposing the charcoal of different woods to air, Allen and Pepys affected by texture.

* See American Journal of Science, vol. v, vi & viii; also Jour. of the Acad. of Nat. Sci. vol. iv. p. 371.
† Lowitz Crell's Annals, vol. ii. p. 165. ‡ Thomson's Annals, vol. vi.
§ Journal de Physique, 1783, and of M. Rouppe Annales de Chimie, vol. xxxii.

found that they increased very differently in weight. By a week's exposure, charcoal from

| | | | |
|-------------------|---------------|------------------|----------------|
| Lignumvitæ gained | 9,6 per cent. | Beech gained | 16,3 per cent. |
| Fir | 13,0 ditto | Oak | 16,5 ditto |
| Box | 14,0 ditto | Mahogany | 18,0 ditto |

The matter absorbed in these cases consisted principally of aqueous vapour, which is very greedily imbibed by newly-made charcoal.

691. *Carbon and Oxygen*.—There are two compounds of carbon and oxygen; the carbonic acid, and the carbonic oxide.

692. *Carbonic Acid Gas* may be obtained by burning carbon, either pure charcoal or the diamond, in oxygen gas.

Combustion
of the dia-
mond.

693. It is not evident to whom the combustibility of the diamond first occurred; but in the year 1694 the Florentine Academicians proved its destructibility by heat by means of a burning lens. The *products* of its combustion were first examined by Lavoisier in 1772, and subsequently with more precision by Guyton Morveau, in 1785.* In 1797, Mr Tennant demonstrated the important fact, that when equal weights of diamond and pure charcoal were submitted to the action of red hot nitre, the results were in both cases the same; and in 1807 the combustion of the diamond in pure oxygen was found by Messrs Allen and Pepys to be attended with precisely the same results as the combustion of pure charcoal. Hence the inevitable inference that charcoal and the diamond are similar substances in their chemical nature, differing only in mechanical texture.†

* *Annales de Chimie*, xxxi.

Pl. v.

† The apparatus fig. 112 may be conveniently employed for exhibiting the results of the combustion of the diamond. It consists of a glass globe, of the capacity of about 140 cubical inches, furnished with a cap, having a large aperture; the stop-cock, which screws into this cap, has a jet, *a*, rising from it, nearly into the centre of the globe; this is destined to convey a small stream of hydrogen, or other inflammable gas. Two wires, *cc*, terminate at a very little distance from each other, just above this jet, and are intended to inflame the stream of hydrogen by electrical sparks; one of them commences from the side of the jet, the other is enclosed and insulated nearly in its whole length in a glass tube: the tube and wire pass through the upper part of the stop-cock, and the wire terminates on the outside in a ball or ring, *d*, at which sparks are to be taken from the machine, either directly or by a chain. On the end of the jet is fixed, by a little socket, a small capsule, *b*, made of platinum foil. This capsule is pierced full of small holes, and serves as a grate to hold the diamonds. Its distance is about three-quarters of an inch from the end of the jet; and the arm, by which it is supported, is bent round, so that the stream of hydrogen shall not play against it. The stop-cock screws, by its lower termination, on to a small pillar, fixed on a stand, and at the side of this pillar is an aperture by which a bladder filled with gas may be connected with the apparatus.

On using the apparatus, the diamond is to be placed in the capsule; and then the globe being screwed on to the stop cock, the latter is to be removed from the pillar and placed on the air pump; the globe is then to be exhausted, and afterwards filled with pure oxygen: or, lest the stream of oxygen in entering should blow away the diamond, the globe may be filled with the gas first, and then, dexterously taking out the stop-cock for a short time, the diamonds may be introduced and the stop-cock replaced. The apparatus is then to be fixed on the pillar, and a bladder of hydrogen gas attached to the aperture. Now, passing a current of sparks between the wires, a small stream of hydrogen is to be thrown in, which inflaming, immediately heats the capsule and diamonds white hot; the diamonds will then enter into combustion, and the hydrogen may be immediately turned off and the bladder detached. The diamonds will continue to burn, producing a strong white heat, until so far reduced in size as to be cooled too low by the platinum with which they lie in contact.

694. Messrs Allen and Pepys collected the product of the combustion of charcoal and of the diamond, by means of the apparatus represented by fig. 113.* *a a* are mercurial gasometers, one of which is filled with pure oxygen gas. The brass tubes *b b*, properly supplied with stopcocks, issue from the gasometers, and are connected with the platinum tube *c c*, which passes through the small furnace *d*. *e* is a glass tube passing into the mercurio-pneumatic apparatus by which the gas may be drawn out of the gasometers into convenient receivers. A given weight of diamond is introduced into the centre of the platinum tube, which is then heated to bright redness, and the gas passed over it, backwards and forwards, by alternately compressing the gasometers. Carbonic acid is soon formed, and it will be found that the increase of weight sustained by the oxygen is equivalent to that lost by the diamond; that the oxygen undergoes no change of bulk; and that the results are, in all respects, similar to those obtained by a similar combustion of perfectly pure charcoal.

Allen and
Pepys's ap-
paratus.
Pl. v.

695. From the quantity of charcoal or diamond consumed in the experiments of Allen and Pepys, and the quantity of oxygen converted into carbonic acid, it is easy to infer the proportion of carbon and oxygen in the new compound. Reducing these to centesimal proportion for every 28 or 29 grains of the combustible base which disappeared, 100 grains of carbonic acid (= about 201 cubic inches) were generated; and it is remarkable that these proportions agree exactly with those originally stated by Lavoisier. The same quantity of carbonic acid resulted, also, from the combustion of between 28 and 29 grains of diamond. Hence it may be inferred, that the actual quantity of carbon in equal weights of diamond and charcoal is very nearly the same; and that charcoal is not, as has hitherto been supposed, an oxide of carbon; their only difference consisting in the presence of hydrogen in charcoal, in so small proportion as not materially to diminish the quantity of carbonic acid produced by its combustion. If this inference required confirmation, it is furnished by its agreement with Mr Tennant's experiments on the combustion of the diamond, published in 1797. Two grains and a half of diamond, (this philosopher found), when consumed in a tube of gold by means of nitre, give nine grains of carbonic acid, which, in 100 parts, should contain, therefore, as nearly as possible, 28 parts of diamond or carbon. The mean of a number of Messrs Allen and Pepys' experiments give the following statement of the composition of carbonic acid:

Results.

| | | | |
|------------------|-------|-----------|-------|
| Carbon | 28,60 | | 100 |
| Oxygen | 71,40 | | 250 |
| | | | <hr/> |
| | | | 100. |

696. Mr Dalton assumes the composition of carbonic acid to be in round numbers, 28 of charcoal and 72 of oxygen; from

Composition
of Carbonic
acid.

* *Phil. Trans.* 1807.

whence he deduces the weight of the atom of charcoal to be 5.4. But if the atom of oxygen weigh 8, and if the proportions just assigned be correct, the atom of charcoal will weigh 6, and that of carbonic acid (considering it as a ternary compound of two atoms of oxygen and one of charcoal) will be $16 + 6 = 22$. In volumes, its constitution has been stated by Gay-Lussac to be 1 volume of gaseous carbon + 1 of oxygen, condensed into the space of 1 volume, and the density of the vapour of charcoal has been estimated to be equal to the density of carbonic acid, less than that of oxygen gas, or to $1,5277 - 1,1111 = 0,4166$.*

697. When one volume of carbonic oxide is converted into carbonic acid we add half a volume of oxygen and obtain one volume of carbonic acid, which gas may therefore be considered as constituted either of one volume of carbonic oxide + half a volume of oxygen condensed into one volume, or of one volume of vaporous carbon + 1 volume of oxygen, condensed into 1 volume.

Proofs from
analysis.

698. In addition to the proofs of the constitution of carbonic acid derived from its synthesis, we have also the evidence of its analysis, which may be effected by several processes.

1. By passing a succession of electrical discharges through a quantity of carbonic acid gas confined over mercury, Dr Henry has found that the gas is separated into oxygen, and carbonic oxide. When the carbonic acid, which escapes decomposition, has been washed out by a solution of potassa, an electric spark inflames the residuary mixture; the oxygen and carbonic oxide again uniting, and re-composing carbonic acid.†

2. When a mixture of carbonic acid and hydrogen gases is electrified, the hydrogen combines with part of the oxygen of the acid, and reduces it to the state of carbonic oxide. The same products are obtained, by transmitting a mixture of two parts of hydrogen gas and one of carbonic acid through a glazed porcelain tube strongly ignited. The hydrogen, uniting with a part of the carbonic acid, brings the latter to the state of carbonic oxide, at the same time that water is formed. H. 1 345.

699. It may also be analyzed by the action of the metal *potassium*, which is capable of abstracting its oxygen, and, with the aid of heat, burns in it with great splendour; charcoal is deposited, and an *oxide of Potassium* is formed. In this and in some other cases, oxygen is seen alternately producing acid and alkali. If carbonic acid, obtained by burning the diamond in oxygen, be thus decomposed by potassium, the carbon makes its appearance in the form of charcoal, equal in weight to the diamond consumed.

700. Carbonic acid is a most abundant natural product; the best mode of procuring it for experiment consists in acting upon marble (*carbonate of lime*) by dilute muriatic acid.

| | | |
|--------------------------------------|---------|---------------|
| * Sp. gr. of Carbon vapour | 0.375 | } Oxygen = 1. |
| " " " Carbonic acid | 1.375 | |
| Atomic weight of ditto | 2.75 | |
| Weight of 100 cubic inches | 46.5972 | T. |

† *Phil. Trans.* 1809, 448.

For this purpose the marble, in small fragments, is introduced into the two-necked bottle *a*, fig. 114, and covered with water; muriatic acid is then slowly poured down the funnel *b*, which causes an immediate effervescence, and the gas passes through the bent tube *c*, into the inverted jar *d*. When the action ceases, it may be renewed by the addition of fresh acid, until the whole of the marble is dissolved.

Method of obtaining carbonic acid.

Pl. v.

As carbonic acid gas is heavier than atmospheric air it may also be obtained by means of the apparatus fig. 115, *a* is a long glass tube proceeding from the bottle containing the marble and acid, and passing down to the bottom of the jar *b*, which stands with its mouth uppermost. The carbonic acid will expel the common air from the jar.

701. Carbonic acid may be collected over water, but must be preserved in vessels with glass-stoppers, since water, at common temperature and pressure, takes up its own volume.

Absorbed by water.

Fill partly a jar with this gas, and let it stand a few hours over water. An absorption will gradually go on, till at last none will remain. This absorption is infinitely quicker when agitation is used. Repeat the above experiment, with this difference, that the jar must be shaken strongly. A very rapid diminution will now take place. In this manner, water may be charged with rather more than its own bulk of carbonic acid gas; and it acquires, when thus saturated, a very brisk and pleasant taste.

Exp.

702. The effervescent quality of many mineral waters is referable to the presence of this gas, and they are often imitated by condensing carbonic acid into water, either by a condensing pump, of which a description is given by Mr Pepys,* or by a Nooth's apparatus, as represented in fig. 116.†

Pl. v.

Under a pressure of two atmospheres water dissolves twice its volume of this gas, and so on. It thus becomes brisk and tart, and reddens delicate vegetable blues. By freezing, boiling or exposure to the vacuum of the air-pump, the gas is given off.

Place a tumbler of water which has been impregnated with this gas (the soda water of the shops, for example) under the receiver of the air-pump, and exhaust it; the gas will escape so rapidly as to prevent the appearance of ebullition; and will be much more remarkable than the discharge of air from another vessel of common spring water, confined at the same time under the receiver.

Exp.

703. If the impregnated water be rapidly congealed, by surrounding it with a mixture of snow and salt, the frozen water has more the appearance of snow than of ice, its bulk being prodigiously increased by the immense number of air bubbles.

Expelled by freezing.

* *Quarterly Journal of Science and the Arts*, vol. iv. p. 305.

† It consists of three vessels, the lowest, *a*, flat and broad, so as to form a steady support; it contains the materials for evolving the gas, such as pieces of marble and dilute muriatic acid, of which fresh supplies may occasionally be introduced through the stopped aperture. The gas passes through the tube *b*, in which is a glass valve opening upwards, into the vessel *c*, containing the water or solution intended to be saturated with the gas, and which may occasionally be drawn off by the glass stop-cock. Into this dips the tube of the uppermost vessel *d*, which occasions some pressure on the gas in *c*, and also produces a circulation and agitation of the water. At the top of *d* is a conical stopper, which acts as an occasional valve, and keeps up a degree of pressure in the vessels.

When water, thus congealed, is liquefied again, it is found, by its taste, and other properties, to have lost nearly the whole of its carbonic acid.

Fatal to animals.
Exp.

704. Carbonic acid gas is unrespirable, and is fatal to animals.

Put a mouse or other small animal into a vessel of the gas, and cover the vessel to prevent the contact of common air; the animal will die in the course of a minute or two.*

Does not support combustion.

705. It extinguishes flame.

This may be shown by setting a vessel filled with the gas, with its mouth upwards, and letting down a lighted candle. The candle will be instantly extinguished.

Exp.

The experiment may be varied by placing near the vessel containing the carbonic acid gas, a similar one filled with oxygen gas, and if the candle after being extinguished by the carbonic acid be speedily immersed in the oxygen gas it will be relighted, and this may be repeated as long as the gases remain in the vessels.

Heavier than atmospheric air.

706. Carbonic acid gas is heavier than atmospheric air, and may be poured from one vessel into another like water.

Exp.

Place a lighted taper at the bottom of a tall glass jar, and pour the gas out of a bottle into it; it descends and extinguishes the flame, and will remain a long time in the lower part of the jar.

Hence in wells and in some caverns, carbonic acid gas frequently occupies the lower parts, while the upper parts are free from it. Hence also the precaution used by the sinkers of wells, of letting down a candle before they venture to descend in person. The miners call it *choak damp*.

Possesses acid properties.

707. When combined with water this gas reddens vegetable colours. This may be shown by dipping into water, thus impregnated, a bit of litmus paper, or by mixing, with a portion of it about an equal bulk of the infusion of litmus. This fact establishes the title of the gas to be ranked among acids. When an infusion of litmus which has been thus reddened, is either heated, or exposed to the air, its blue colour is restored, in consequence of the escape of the carbonic acid. This is a marked ground of distinction from most other acids, the effect of which is permanent, even after boiling.

Test of its presence.

Exp.

Carbonic acid gas precipitates lime-water—this character of the gas is necessary to be known, because it affords a ready test of the presence of carbonic acid, whenever it is suspected. Pass the gas as it proceeds from the materials, through a portion of lime water. This, though perfectly transparent before, will instantly grow milky: Or, mix equal measures of water saturated with carbonic acid, and lime water. The same precipitation will ensue. By means of lime-water, the whole of any quantity of carbonic acid, existing in a mixture of gases, cannot, however, be removed, as Saussure, jun. has shown; but recourse

* By means of this gas, butterflies, and other insects, the colours of which it is desirable to preserve, for the purpose of cabinet specimens, may be suffocated better than by the common mode of killing them by the fumes of sulphur. H.

must be had in order to effect an entire absorption, to a solution of caustic potassa or soda.*

As all common combustibles, such as coal, wood, oil, wax, tallow, &c. contain carbon as one of their component parts, so the combustion of these bodies is always attended by the production of carbonic acid. A product of combustion.

1. Let the chimney of a portable furnace, in which charcoal is burning, terminate, at a distance sufficiently remote to allow of its being kept cool, in the bottom of a barrel, provided with a moveable top, or of a large glass vessel, having two openings. A small jar of lime-water being let down into the tube or vessel, and agitated, the lime-water will immediately become milky. The gas will also extinguish burning bodies, and prove fatal to animals that are confined in it. Exp.

Hence the danger of exposure to the fumes of charcoal, which, in several instances have been known to be fatal. These fumes consist of a mixture of carbonic acid and nitrogen gases with a very small proportion of oxygen gas.

2 Fill the pneumatological trough with lime-water, and burn a candle, in a jar filled with atmospheric air, over the lime water till the flame is extinguished. On agitating the jar, the lime water will become milky. The same appearances will take place, more speedily and remarkably if oxygen gas be substituted for common air. Exp.

The carbonic acid, thus formed during combustion, by its admixture with the residuary air, renders it more unfit for supporting flame, than it otherwise would be from the mere loss of oxygen. Hence, if a candle be burnt in oxygen it is extinguished long before the oxygen is totally absorbed; because the admixture of carbonic acid with oxygen gas, in considerable proportion, unfits it for supporting combustion. Whenever any substance, by combustion in oxygen gas or common air over lime water, gives a precipitate, soluble with effervescence in muriatic acid, we may infer that it contains carbon. H. 1. 351.

708. It is also produced by the respiration of animals; hence it is detected often in considerable proportion, in crowded and illuminated rooms, which are ill ventilated, and occasions difficulty of breathing, giddiness, and faintness. And of respiration.

The production of carbonic acid, by respiration, may be proved by blowing the air from the lungs, with the aid of a quill, through lime water, which will become milky. Exp.

709. In the atmosphere it may also be detected, varying in quantity from 1 to 0,1 per cent.

710. Carbonic acid retards the putrefaction of animal substances. This may be proved, by suspending two equal pieces of flesh meat, the one in common air, the other in carbonic acid gas, or in a small vessel through which a stream of carbonic acid is constantly passing. The latter will be preserved untainted some time after the other has begun to putrefy. Retards putrefaction.

711. Carbonic acid gas exerts powerful effects on living vegetables. These effects, however, vary according to the mode of its Its effect on vegetables.

* If excess, either of the gas or of its aqueous solution, be added to the lime water, the precipitate is re-dissolved, carbonate of lime being soluble in carbonic acid.

application. Water saturated with this gas, proves highly nutritive, when applied to the roots of plants. The carbonic acid is decomposed, its carbon forming a component part of the vegetable, and its oxygen being liberated in a gaseous form.

On the contrary, carbonic acid, when a living vegetable is confined in the undiluted gas over water, is injurious to the health of the plant, especially in the shade. The late Mr Henry long ago found, that a certain quantity of this gas, applied as an atmosphere, is favourable to vegetation; and M. Saussure of Geneva, has determined more recently that the mixture of more than $\frac{1}{8}$ of carbonic acid with common air is always injurious; but that, in this proportion, it produces the growth of plants, and is manifestly decomposed.

712. It is this process of nature that appears to be the principal means of preventing an excess of carbonic acid in the general mass of the atmosphere, which, without some provision of this kind, must gradually, in the course of ages, be rendered less and less fit for respiration. H. 1. 353.

Liquefaction
of carbonic
acid.

713. Carbonic acid has been obtained in a liquid form by Mr Faraday. The materials used, were carbonate of ammonia and concentrated sulphuric acid; the manipulation was like that described for sulphuretted hydrogen. Much stronger tubes are however required for carbonic acid than for any of the substances already noticed, and there is none which has produced so many or more powerful explosions. Tubes which have held fluid carbonic acid well for two or three weeks together, have, upon some increase in warmth of the weather, spontaneously exploded with great violence; and the precaution of glass masks, goggles, &c. which are at all times necessary in pursuing these experiments, are particularly so with carbonic acid.

Characters.

714. Carbonic acid is a limpid colourless body, extremely fluid, and floating upon the other contents of the tube. It distils readily and rapidly at the difference of temperature between 32° and 0° . Its refractive power is much less than that of water. No diminution of temperature to which it was submitted, altered its appearance. In endeavouring to open the tubes at one end, they uniformly burst into fragments with powerful explosions.

Its vapour exerted a pressure of thirty-six atmospheres, at a temperature of 32° .*

Carbonates:

715. Carbonic acid combines with alkalis, earths and metals, and the compounds are termed *carbonates*: as it is usually retained in combination by very feeble affinity, so it is evolved from most of the carbonates by the simple operation of heat. Thus chalk, when heated, gives out carbonic acid, and becomes *quicklime*. It is also evolved from its combinations by most of the other acids; and if nitric, muriatic, or sulphuric acid, be poured upon the carbonates, the presence of carbonic acid is indicated by *effervescence*.

Efferves-
cence.

* Faraday, *Phil. Trans.*

716. If carbonic acid be passed over red-hot charcoal, it becomes converted into carbonic oxide by taking up an additional proportion of base. The blue flame, often seen upon the surface of a charcoal fire, arises from the combustion of the carbonic oxide formed in this way; the air entering at the bottom, forms carbonic acid, which, passing through the red-hot charcoal, becomes converted into carbonic oxide.

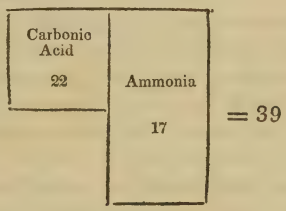
717. At a bright red heat, iron decomposes carbonic acid, by abstracting a portion of its oxygen, and forming oxide of iron and carbonic oxide.

718. *Carbonic Acid and Ammonia.*—These gases readily combine, and produce one of the most useful and best known of the ammoniacal compounds. When one volume of carbonic acid gas and two volumes of ammonia are mixed in a glass vessel, over mercury, a complete condensation ensues, and *carbonate of ammonia* is produced.

As 100 cubic inches of carbonic acid weigh 46,56 grains, and 200 of ammonia 36,36 grains, in all 82,92 grains, carbonate of ammonia must consist of

| | | Atoms. | |
|---------------|-------|--------|----|
| Carbonic acid | 56,20 | 1 | 22 |
| Ammonia | 43,80 | 1 | 17 |
| | 100, | | 39 |

It may be represented thus

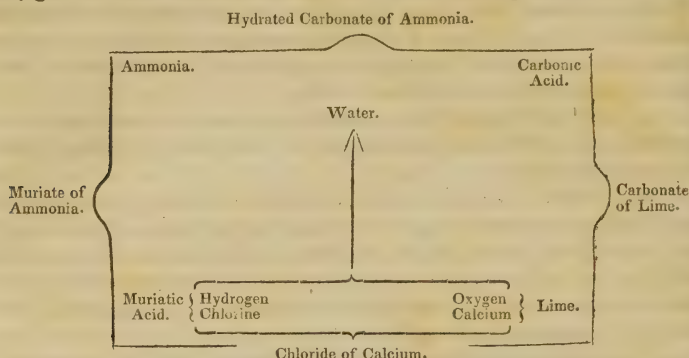


719. If water be present, it so far overcomes the elasticity of the gas, as to enable the salt formed to take up another volume of carbonic acid, and thus a *bicarbonate* is formed.

720. Carbonate of ammonia crystallizes in octoëdrons though it is generally met with in cakes broken out of the subliming vessel, being obtained by sublimation from a mixture of muriate of ammonia and carbonate of lime.

The results, however, of this decomposition are not strictly speaking, carbonate of ammonia and muriate of lime, but carbonate of ammonia, water, and chloride of calcium, the two former being in combination, so that a *hydrated carbonate of ammonia* is always obtained.

Supposing the materials perfectly dry, the water is formed by the union of the hydrogen of the muriatic acid with the oxygen of the lime, as shown in the following diagram :



Sesqui-car-
bonate of am-
monia.

721. *Sesqui-carbonate of Ammonia*.—Mr Phillips has shown* that the carbonate of ammonia of commerce (*ammonia sub-carbonas* of the Lond. Pharmacopœia) is a compound of

| | |
|--|-------------|
| 3 Proportionals of Carbonic acid | 22 × 3 = 66 |
| 2 Ditto Ammonia | 17 × 2 = 34 |
| 2 Ditto Water | 9 × 2 = 18 |

118

Viewing it as a compound of $1\frac{1}{2}$ proportions of carbonic acid, 1 ammonia, and 1 of water, it has been called by Mr Phillips a *sesqui-carbonate*, and if this view be unconnected with the notion of its containing the fraction of an atom, there can be no objection to the name. It is preferable, indeed, to that of subcarbonate, which should be reserved for the compound, of 1 atom of acid and 2 of base.

Properties.

722. When the sesqui-carbonate is fresh prepared, it has a crystalline appearance and some transparency, and is hard and compact. It has a pungent smell, and a sharp penetrating taste, and affects vegetable blues as uncombined alkalies do. It dissolves in twice its weight of cold or an equal weight of boiling water. When exposed to the atmosphere, it loses weight very fast, ceases to be transparent, loses its odour, becomes brittle and easily reducible to powder; (H. 1. 418.) and ceases to act upon turmeric paper. In this state it may be considered as an *hydrated bicarbonate of ammonia*, and is composed, according to Phillips, of

Composition.

| | |
|--|-------------|
| 2 Proportionals of Carbonic acid | 22 × 2 = 44 |
| 1 Ditto Ammonia | = 17 |
| 1 Ditto Water | 9 × 2 = 18 |

79 B.

It has therefore lost, by exposure, 1 atom of acid and one atom of base.

723. By varying the proportions of the ingredients, and the regulation of the heat, it is possible to obtain a bi-carbonate at once by sublimation.*

724. *Carbonic Oxide* is usually obtained by subjecting carbonic acid to the action of substances which abstract a portion of its oxygen. Upon this principle, carbonic oxide gas is produced by heating in an iron retort a mixture of chalk and charcoal; or of equal weights of chalk and iron or zinc filings. It is also obtained by the distillation of the white oxide of zinc with one-eighth of its weight of charcoal, in an earthen or glass retort; from the scales which fly from iron in forging, mixed with a similar proportion of charcoal; from the oxides of lead, manganese, or, indeed, of almost every imperfect metal, when heated in contact with powdered charcoal. It may also be obtained from the substance which remains after preparing acetic acid from acetate of copper. But the mixture that affords it most pure, is equal parts of carbonate of baryta and clean iron filings; these should be introduced into a small earthen retort, so as nearly to fill it, and exposed to a red heat: the first portion of gas being rejected as mixed with the air of the retort, it may afterwards be collected quite pure.

Carbonic oxide.

How obtained.

It may also be obtained by transmitting carbonic acid gas over charcoal ignited in a porcelain tube. The acid gas combines with an additional dose of charcoal; loses its acid properties; and is converted into carbonic oxide.†

725. The nature of this gas was first made known by Mr Cruickshank, of Woolwich, in 1802‡ and about the same time it was examined by Messrs Clement and Desormes.§

726. It is lighter than common air in the proportion of 0,9722 according to Thomson, or 0,9727 according to Berzelius and Dulong: 100 cubical inches weigh 30,19 grains at 60° F. and barometer 30. Its specific gravity to hydrogen is as 14 to 1.

Properties.

It extinguishes flame, and burns with a pale blue lambent light, when mixed with, or exposed to atmospheric air. The temperature of an iron wire heated to dull redness was found by Sir H. Davy sufficient to kindle it. A mixture of two measures with one of common air may be exploded by a lighted taper, or even by red-hot iron or charcoal. H. 1. 355.

727. It is extremely noxious to animals; and fatal to them if confined in it. When respired for a few minutes, it produces giddiness and fainting.||

* *Annals of Philos.* N. S. iii. 110.

† An ingenious apparatus, contrived by M. Baruel, and extremely useful for this and similar purposes is represented by fig. 111. A is the bottle from which the carbonic acid gas is extricated; C, a tube nearly filled with pieces of chloride of calcium to attract moisture; F, a reverberatory furnace in which three gun barrels *x x' x''* are placed, containing the charcoal, and communicating with each other by glass tubes *d d'*; *m*, the tube that conveys the carbonic acid gas into the first gun barrel *x*; lastly, *t t*, the bent tube by which the carbonic oxide produced, passes. The last product of the distillation is the purest, but still contains carbonic acid, which must be separated by washing the gas with lime liquor.

Pl. v.

‡ Nicholson's 4to *Journal*, v.

§ *Annales de Chimie*, xxxix.

|| See *Phil. Mag.* xliii. 367.

728. When a stream of carbonic oxide is burnt under a dry bell-glass of air or oxygen, no moisture whatever is deposited, showing, that it contains no hydrogen.

Detonates
with oxygen.

729. When two volumes of carbonic oxide, and one of oxygen, are acted on by the electric spark, a detonation ensues, and two volumes of carbonic acid are produced. Whence it appears, that carbonic acid contains just twice as much oxygen as carbonic oxide, which may be considered as a compound of one volume of oxygen and one volume of gaseous carbon; or of one proportional of carbon and one of oxygen, the latter being so expanded as to occupy two volumes.

Decomposi-
tion,

730. Carbonic oxide suffers no change by being passed and repassed through a red-hot porcelain tube; nor is it decomposed at high temperatures by phosphorus, sulphur, nor even, according to the experiments of Saussure, by hydrogen.* But when previously mingled with an equal bulk of hydrogen gas, and passed through an ignited tube, the tube becomes lined with charcoal. In this temperature, the hydrogen attracts oxygen more strongly than it is retained by the charcoal, and water is formed.

by potassium,
sodium,

731. None of the metals exert any action upon this gas, except potassium and sodium, which at a red heat, burn in it by abstracting its oxygen, and carbon is deposited.

and spongy
platinum.

732. When a mixture of carbonic oxide with more than half its volume of oxygen gas, is exposed over mercury, in contact with spongy platinum, to a temperature between 300° and 310° F. it begins to be converted into carbonic acid, and at a heat of a few degrees higher is wholly acidified in the course of a few minutes. Mixtures of these two gases are, however, very slowly acted upon by the platinum sponge at common temperatures.

When carbonic oxide is added, in an equal volume, to a mixture of hydrogen and oxygen gases in explosive proportions, it prevents spongy platinum from causing detonation, but the agency of the gases on each other goes on slowly, and both water and carbonic acid are formed. Into a mixture of carbonic oxide with a larger proportion of the explosive mixture, the platinum sponge cannot be introduced without causing detonation.†

Composition.

733. According to Mr Cruickshank, it contains per cent. about 70 oxygen, and 30 carbon by weight: or the former is to the latter as 21 to 8,6, or as 21 to 9. Gay-Lussac however, makes it to consist of 43 charcoal and 57 oxygen; Berzelius of 44,28 charcoal and 55,72 oxygen, proportions which agree within a small fraction with those of Clement and Desormes. On the theory of volumes, it consists of half a volume of oxygen and 1 volume of gaseous carbon, condensed into 1 volume; and as each of those quantities is equivalent to an atom, it may

* *Journal de Physique*, lv.

† *Phil. Trans.* 1824, p. 271.

be stated to consist of an atom of oxygen = 8 + an atom of charcoal = 6, together 14. Its specific gravity should then be found by adding half the sp. gr. of oxygen to the sp. gr. of gaseous carbon, viz. $0,4166 + 0,5555 = 0,9721$. H. 1. 356.

734. *Carbon and Chlorine*.—Mr Faraday has ascertained that, by exposing carburetted hydrogen, mixed with great excess of chlorine, to the action of light, a white crystalline substance is formed, which, when purified by washing with water, is a *perchloride of carbon*.* Union of carbon and chlorine.

735. This substance is nearly tasteless; its odour resembles camphor; its specific gravity is about 2; it is a nonconductor of electricity. It is volatile, and in close vessels fuses at 320° , and boils at 360° . It is not very combustible, but burns when held in the flame of a spirit lamp, with the emission of much smoke and acid fumes. It is very sparingly soluble in water, but readily soluble in alcohol and ether; these solutions deposit arborescent and quadrangular crystals. It also dissolves in volatile and fixed oils. It is scarcely acted upon by alkaline and acid solutions; but most of the metals decompose this substance at a red heat. Potassium burns brilliantly in its vapour, causing the deposition of carbon, and the production of chloride of potassium. The metallic oxides also decompose it at high Properties.

* To procure this substance a retort or other glass vessel of the capacity of about 200 cubic inches, provided with a brass cap and stop-cock, is first to be exhausted by the air pump, and then made to communicate with a jar filled with chlorine. It is next to be screwed on a vessel full of olefiant gas, and as much as can find admission having entered, the cock is to be shut, and the whole left for a short time. When the fluid, composed of chlorine and olefiant gases, has formed and condensed on the sides of the vessel, the vessel is again to be placed over olefiant gas, and a further portion admitted. This process is to be repeated, till all the chlorine has united to form the fluid, and the vessel remains full of olefiant gas. Chlorine is then to be admitted by repeated portions, in consequence of which more of the fluid is formed, and ultimately a large portion is obtained, with an atmosphere of chlorine above it. The vessel is now to be exposed to the sun's rays, which cause the immediate formation of muriatic acid gas. This may be absorbed by admitting a small portion of water; and then another atmosphere of chlorine is to be introduced. Again exposed to the light, this will partly combine with the carbon, and partly form muriatic acid gas, which, being, as before, absorbed by water, leaves space for more chlorine. Repeating this action, the fluid gradually becomes thick and opaque, from the formation of crystals in it, which at last adhere to the sides of the vessel as it is turned round; and ultimately the vessel contains only chlorine, with the accumulated impurities of the gases; a strong solution of muriatic acid coloured blue by its action on the brass; and the solid substance in question. Process.

In order to cleanse the substance, the remaining gases are first to be blown out of the vessel by a pair of bellows, and the vessel is then to be filled with water to wash away the muriatic acid and other soluble matters. The new substance is then to be detached from the inside of the vessel, and poured with the water into a jar. A little alcohol will remove the last portions which adhere to the glass, and, when poured into the water, will precipitate the new compound, which must be collected on a filter and dried as much as possible by pressure between folds of bibulous paper. It must next be introduced into a glass tube, and sublimed by a spirit lamp. A part will be decomposed, and the sublimed portion is to be dissolved in alcohol, and poured into a weak solution of potassa, by which the new substance is thrown down, and the muriatic acid neutralized and separated. Then wash away the potassa and muriate by repeated affusions of water, until the substance remains pure; collect it on a filter and dry it, first by pressure between folds of paper, and afterwards by sulphuric acid under the exhausted receiver of an air pump.

It will now appear as a white pulverulent substance; and, if perfectly pure, will not, when a little is sublimed in a tube, leave the slightest trace of carbon, or afford any muriatic acid. A small portion, dissolved in ether, should give no precipitate with nitrate of silver. If not quite pure, it must be re-sublimed, washed, and dried, as often as is necessary. H. 1. 358.

temperatures, producing metallic chlorides, and carbonic acid or oxide, according to the proportion of oxygen present; no water is produced, showing the absence of hydrogen in the compound.

Theory of its
formation.

736. In forming this substance, Mr Faraday believes that five volumes of chlorine gas saturate one of olefiant, and produce four volumes of muriatic acid gas; that three volumes of the chlorine combine with the two volumes of charcoal existing in the olefiant gas to form the crystalline solid; and that when chlorine acts on the fluid compound of chlorine and olefiant gas, for every volume of chlorine that combines, an equal volume of hydrogen is separated. The results of its decomposition by per-oxide of copper, confirm these views, and tend to establish

Composition.

that the composition of per-chloride is

| | |
|-------------------------------|-------|
| 3 atoms of chlorine | = 108 |
| 2 ditto of carbon | = 12 |

Weight of its atom . . . 120. H. 360.

737. When the above perchloride of carbon is passed through a red-hot tube, containing fragments of rock-crystal to increase the heated surface, it gives off a portion of chlorine, and is converted into a liquid *protochloride of carbon*. It is a limpid colourless fluid, specific gravity 1.55, and not combustible, except retained in the flame of the spirit-lamp, when it burns with a yellow flame, much smoke, and fumes of muriatic acid. It does not congeal at 0° ; it rises in vapour at about 165° . It is insoluble in water, but soluble in alcohol, ether, and the oils. It is not affected by the acids or alkalies, nor at common temperatures, by solutions of silver. It dissolves chlorine, iodine, sulphur, and phosphorus. It affords, when decomposed, 17 carbon + 83 chlorine; whence it may be inferred to consist of

Proto-chlo-
ride of car-
bon.

| | |
|---------------------------------|-------|
| 1 Proportional carbon | = 6 |
| 1 Ditto chlorine | = 36 |
| | <hr/> |
| | 42 |

Sub-chloride
of carbon.

738. *Sub-chloride of Carbon*.—A third compound of chlorine and carbon was brought from Sweden by M. Julin, of Abo, where it had been accidentally formed during the distillation of nitric acid from crude nitre and sulphate of iron. The quantity produced at each process did not exceed a few grains, which condensed in fine white feathery crystals in a glass tube connecting the first and second receiver. Its properties are described by M. Julin as follows:*

Properties.

739. It is white; consists of small soft adhesive fibres; sinks slowly in water; is insoluble in it whether hot or cold; is tasteless; has a peculiar smell, somewhat resembling spermaceti; is not acted upon by concentrated and boiling acids or alkalies, except that some of them dissolve a small portion of sulphur; dissolves in hot oil of turpentine and in alcohol, but most of it

* *Ann. of Phil. N. S.*, i. 216.

crystallizes in needles on cooling; burns in the flame of a lamp with a greenish blue flame, and a slight smell of chlorine; when heated melts, boils, and sublimes between 350° and 450° Fahr., or sublimes slowly at a heat of 250° , forming long needles. Potassium burns with a vivid flame in its vapour, and charcoal is deposited; and a solution of the residuum in nitric acid gives a copious precipitate with nitrate of silver.

740. A small quantity of this substance, having been put into the hands of Messrs R. Phillips and Faraday, has been made by them the subject of analysis. They found that it might readily be purified from sulphur by boiling in liquid potassa, washing in water, drying and subliming, when it formed beautiful acicular crystals, in the form of four-sided prisms.

741. It was decomposed into chlorine and charcoal by being passed over red hot fragments of rock crystal. Its vapour, being detonated over mercury with excess of oxygen, gave carbonic acid gas and chloride of mercury. When heated with phosphorus, iron, or tin, chlorides of those substances were formed, and charcoal deposited. Its analysis was effected in two ways; by being transmitted over ignited peroxide of copper, and over dry quick-lime. Both processes gave results which conspire to show that it is constituted of

| | |
|------------------------------|----|
| 1 atom of chlorine | 36 |
| 2 atoms of carbon | 12 |
| | — |
| Weight of its atom | 48 |

Messrs Phillips and Faraday have not given any name to this compound. It may be called, provisionally, the sub-chloride of carbon.

642. Thus we have three distinct compounds of chlorine and carbon, viz.

| | At. of Chlor. | At. of Carb. |
|------------------------------|---------------|--------------|
| The per-chloride | 3 | + 2 |
| The proto-chloride | 1 | + 1 |
| The sub-chloride | 1 | + 2 |

It is probable that another chloride of carbon will hereafter be found, consisting of two atoms of chlorine and one of carbon.

H. 1. 362.

743. *Chloro-carbonic Acid—Phosgene gas.*—When equal volumes of chlorine and carbonic oxide gases, both previously dried by fused chloride of calcium, are introduced into a flask which has been exhausted of air, and are then exposed to bright sunshine for a quarter of an hour, combination takes place, the colour of the chlorine disappears, and the constituent gases are condensed into half their united volumes. Hence its specific gravity must be equal to the specific gravity of chlorine $2,5 +$ that of carbonic oxide $0,9722 = 3,4722$, and 100 cubic inches must weigh 105,9 grains.* Being produced by the agency of light, it was called by Dr J. Davy *phosgene gas*, but as it

Carbon with
chlorine and
oxygen;
Chloro-car-
bonic acid.

* 105,9020. Sp. gr. 3,125 oxygen = 1. T.

exhibits distinctly acid properties, it has since been better termed *chloro-carbonic acid*. It is constituted of an atom of carbon, an atom of oxygen, and an atom of chlorine. Its equivalent, therefore, is $14 + 36 = 50$.

Properties.

It has a peculiar pungent odour and excites a copious flow of tears. It reddens litmus paper. By contact with water, it is resolved into muriatic and carbonic acid gases. It condenses four times its volume of ammoniacal gas, producing a white neutral salt from which the more powerful acids disengage muriatic and carbonic acids, but acetic acid dissolves it without effervescence. Several of the metals decompose it, and unite with the chlorine, evolving carbonic oxide equivalent in volume to the original gas.

Chloro-carbonic acid gas affords then an example of an acid with a simple base, and two acidifying principles, oxygen and chlorine, which are not often united in the performance of this function. H. 1. 363.

Carbon and Hydrogen.

744. *Carbon and Hydrogen* cannot be made to unite by heating charcoal in hydrogen gas, for the cohesive attraction of the particles of the charcoal prevents the combination. It may be effected, however, by exposing to a high temperature some of the solid and liquid compounds of hydrogen and charcoal, and it is produced also by several natural operations, especially by animal and vegetable putrefaction.

Hitherto only two distinct and well characterized compounds of carbon and hydrogen have been investigated so as fully to satisfy us of their properties and the proportions of their elements. The first is called simply *carburetted hydrogen*, and the second is most commonly known by the name of *olefiant* gas. Besides these a third has been pointed out by Mr Dalton, as entering into the composition of oil and coal gas, to which he proposes that the name of *super-olefiant* gas should be provisionally given. It is probable that besides these, other aëri-form compounds of carbon and hydrogen exist. By the destructive distillation of solid and liquid compounds of carbon and hydrogen, it is seldom that we obtain any one of these gases separately, but in most cases a mixture of two or more. Hence there is an almost infinite variety in the specific gravity and composition of gases thus obtained, which has given occasion to the opinion that charcoal and hydrogen are capable of combining in every proportion. There can be no doubt, however, that these apparently numerous compounds are mixtures of a few only; and that combinations of charcoal and hydrogen take place in definite proportions only, with this peculiarity, that they differ from each other not so much in the relative proportions of their elements, as in the numbers of volumes or atoms condensed into a given volume. H. 1. 421.

745. *Carburetted hydrogen* is sometimes called *heavy inflammable air*, *gas of marshes*, *hydro-carburet*, *proto-carburet* of hydrogen, and has been termed by Dr Thomson

bi-hydroguret of carbon. This gas may be collected, mixed however with carbonic acid, and nitrogen gases, by stirring the bottom of almost any stagnant pool of water, especially if formed of clay. It should be washed when collected with lime water or liquid potassa.*

746. Carburetted hydrogen is permanent over water; it has very little odour and its specific gravity is 0,555, hence 100 cubic inches weigh 16,95 grains. When set on fire as it issues from a small orifice, it burns with a yellow flame, giving out vastly more light than hydrogen gas. Properties.

747. Mixed with atmospheric air it may be kindled by a lighted taper, and it explodes with violence, provided it forms not less than $\frac{1}{12}$ th of the mixture, and does not exceed $\frac{1}{6}$ th. With oxygen gas the detonation is louder and more violent; but it is necessary that the oxygen should rather exceed the inflammable gas in volume, and yet should not be more than $2\frac{1}{4}$ times its bulk. For its perfect combustion more than twice its volume of oxygen gas is required, of which exactly two volumes are consumed, and carbonic acid is produced, equivalent in volume to the inflammable gas. Detonation with air, and oxygen gas.

748. It is composed of 2 volumes of hydrogen and 1 volume of gaseous carbon, condensed into 1 volume. But 1 volume of hydrogen requiring half a volume of oxygen to form water, the atomic constitution of carburetted hydrogen will be 1 atom of charcoal (= 6) + 2 atoms of hydrogen (= 2) and the compound atom will weigh 8. From this view of its constitution the name proposed by Dr Thomson is most appropriate. H. 1. 423. Composition.

749. Chlorine and carburetted hydrogen do not act on each other at common temperatures, when quite dry, even if they are exposed to the direct solar rays. If the gases are moist, and the mixture is kept in a dark place, still no action ensues; but if light be admitted decomposition follows. The nature of the products depends on the proportion of the gases. If 4 measures of chlorine and 1 of carburetted hydrogen are present, carbonic and muriatic acid gases will be produced. When 3 measures of chlorine are present carbonic oxide is formed, one half less water being decomposed. H. Action of chlorine.

750. When a mixture of chlorine and carburetted hydrogen are electrized or exposed to a red heat, muriatic acid is formed, and charcoal deposited.

751. *Bi-carburetted Hydrogen—Olefiant Gas.*—This gas was discovered in 1796, by some associated Dutch chemists, and was termed by them olefiant gas, from its property of forming an oily looking liquid with chlorine. It has since been called *bi-carburetted* or *per-carburetted* hydrogen, and by Dr Thomson *hydroguret of carbon*. Bi-carburetted hydrogen.

752. It is usually obtained by the decomposition of alcohol by sulphuric acid. For this purpose four parts of the acid and How obtained.

* Mr Brande considers this and the varieties to be hereafter described as mixtures of olefiant gas and hydrogen;

one of alcohol are put into a retort, and heated by a lamp. Soon after the mixture boils the gas is evolved. It may be collected over water; its specific gravity to hydrogen is 14. 100 cubic inches weigh 29.64 grains.

Properties.

753. This gas is inflammable, burning with a bright yellowish white flame. When mingled with oxygen gas, it explodes with great violence. One part by volume requires, for perfect combustion, three of oxygen; and two of carbonic acid are produced. But to insure the perfect combustion of the inflammable gas, it should be mixed with 5 times its bulk of oxygen, of at least 90 per cent. purity.

Composition

754. Calculating the constitution of this gas, from the oxygen spent in its combustion and the carbonic acid formed, Dr Henry states its composition as follows,

| | | | | |
|--|-------------------|------------------|-----------------|----------------|
| | Vols. of Carb. | Vols. of Hyd. | At. of Carb. | At. of Hyd. |
| In each volume } of olefiant gas. } | 2 | 2 | = | 2 + 2 |

Weight of the atom of olefiant gas $12 + 2 = 14$.

Action of
chlorine,

755. When olefiant and chlorine gases are mixed together in equal quantities, an immediate diminution ensues; and this effect takes place, even when the vessel is shaded from the light by an opaque cover. It is therefore wholly independent of the agency of light and may be made the basis of a method of analyzing a mixture of olefiant and carburetted hydrogen gases. For of the diminution thus produced, one half is due to the olefiant; and one half to the chlorine; those gases having been ascertained to saturate each other in equal volumes.*

origin of the
name.

756. By the action of chlorine gas, a liquid substance is formed, in appearance very much resembling oil, and which, being at first mistaken for oil, occasioned this gas to be called olefiant. It possesses however, very different properties from those of oil, and more nearly approaches in character to ether. It may be collected by using large quantities of the two gases, taking care to have an excess of olefiant gas, and it may be purified by washing it with water, and then distilling it from dry chloride of calcium.

Chloric ether.

757. It has an agreeable ethereal smell, and a not unpleasant taste. Its specific gravity at 45° F. is 1.2201; it boils at 152° . It consists of 1 vol. of chlorine + 1 vol. of olefiant gas condensed into 1 vol. or of 2 atoms of olefiant gas + 1 atom of chlorine. It has been called by Dr Thomson *chloric ether*, but a more appropriate name would be *hydro-chloride of carbon*.

758. When olefiant gas is mixed with eight or nine times its bulk of chlorine, and exposed to the sun's rays, at first the fluid hydro-chloride of carbon is formed, and this, by continuing the exposure, is changed into per-chloride of carbon.

Hydriodide of
carbon.

759. When iodine and olefiant gas are exposed to the action of light they combine, and form a *hydriodide of carbon*. This compound was first obtained by Mr Faraday. It is a white

* For the details of this process, see Henry's *Chemistry*, Edit. 10th, vol. 1. p. 426.

crystalline solid, volatile and in many respects analogous to the hydrochloride of carbon. It appears to consist of 1 atom of iodine + 2 atoms of olefiant gas.*

760. M. Serrulas has also discovered a compound of olefiant gas and iodine. It has a yellow colour like sulphur, and forms scaly crystals of a pearly lustre. It was originally prepared by adding potassium to a solution of iodine in alcohol; but has been since made by mixing a solution of pure potassa in alcohol with an alcoholic solution of iodine. The object of both processes being to present iodine in solution to olefiant gas in a nascent state.†

761. Mr Dalton has given the name of *Super-olefiant gas*, Super-olefiant gas. to a gas not yet exhibited in a separate form but mingled with others in the æriform products of coal, oil, &c. According to the experiments of Dr Henry it probably consists of 3 vols. of gaseous carbon and 3 vols. of hydrogen condensed into 1 volume.‡

762. The gases above described are abundantly produced Coal-gas. during the destructive distillation of common pit-coal; and the gas thus obtained is employed for the purposes of illumination, as an economical substitute for tallow, oil, &c. The coal is placed in oblong cast-iron cylinders, or retorts, which are ranged in furnaces to keep them at a red heat, and all the volatile products are conveyed by a common tube into a *condensing vessel*, kept cold by immersion in water; and in which the water, tar, ammoniacal, and other condensable vapours, are retained; the gaseous products consist principally of carburetted hydrogen, sulphuretted hydrogen, and carbonic oxide and acid; these are passed through a mixture of quicklime and water in vessels called *purifiers*, by which the sulphuretted hydrogen and carbonic gases are absorbed, and the carburetted hydrogen and hydrogen gases, transmitted sufficiently pure for use into *gasometers*, whence the pipes issue for the supply of streets, houses, &c. The coke remaining in the retorts is of a very good quality.

763. The specific gravity of coal-gas varies from 0,443 to 0,700. 100 cubical inches weigh from 14 to 15 grains, and it Specific gravity. may be considered as a mixture of about 55 volumes of hydrogen, and 45 of olefiant gas.

764. The best kind of coal for distillation is that which contains most bitumen and least sulphur; 112 pounds of good coal are capable of yielding from 450 to 500 cubic feet of gas of such quality, that half a cubic foot per hour is equivalent to a mould candle of six to the pound, burning the same space of time. H.

765. Messrs J. and P. Taylor have constructed an apparatus Oil gas. for the conversion of oil into gas. It consists of a furnace with a contorted iron tube containing fragments of brick or coke, passing through it, into which, when red hot, the oil is suffered to drop; it is decomposed, and converted almost entirely into

* *Quart. Jour.* xiii. 429.† *Ann. de Chem. et de Phys.* xx. and xxii.‡ *Phil. Trans.* 1821, 156.

charcoal, which is deposited in the tube, and into a mixture of carburetted hydrogen, and hydrogen gases, of which one volume may be regarded as equivalent to two of coal-gas, for the production of light.*†

The commonest whale oil, quite unfit for burning in the usual way, affords abundance of excellent gas, requiring no other purification than passing through a refrigerator to free it from a quantity of empyreumatic vapour.

766. A gallon of whale-oil affords about 100 cubical feet of gas, and an Argand burner, equal to seven candles, consumes a cubical foot and a half per hour.

Its fitness for
illumination
determined.

767. The fitness of the gas obtained from coal for the purposes of illumination, is, *ceteris paribus*, dependent upon the quantity of carburetted hydrogen, or olefiant gas, which it contains; and, consequently, the fitness of the purified mixed gas for illumination, will be directly as its specific gravity; or, the relative proportion of olefiant gas, may be judged of by mixing the purified coal gas with twice its volume of chlorine over water, by which the olefiant gas will be absorbed, and its quantity shown by the amount of the absorption which takes place.

Dr Henry‡ has given some important experiments upon the production of gas from coal, by which it appears that its composition is various at different stages of the distillation. The mode of distillation also affects the quantity and quality of the products.§||

768. A mixture of carburetted hydrogen and hydrogen is contained abundantly in coal strata, from fissures in which it is sometimes evolved in large quantities, forming what in the language of the miners, is called a *blower*. When this gas is accumulated in any part of the gallery or chamber of a mine, so as to be mixed in certain proportions with common air, the presence of a lighted candle, or lamp, causes it to explode, and to destroy, injure, or burn whatever is exposed to its violence. The miners are either immediately killed by the explosion, and thrown with the horses and machinery, through

* *Quarterly Journal*, vol. viii.

† A few years since I constructed an apparatus which I find exceedingly convenient for obtaining oil gas, in sufficient quantity for the exhibition of its properties, it is represented by fig. 117. *a* is a vessel of cast iron about 16 inches in depth, and 6 in diameter at its upper part; having a cast iron cover, with two openings, to the smallest of which, a copper pipe leading from a funnel-shaped oil vessel *b*, is secured by brazing; into the larger opening a gun barrel *c* is screwed which enters a small copper condensing vessel *d* furnished with a cock for drawing off any oil, or condensable vapours that may pass over. From the upper part of the condenser a copper or lead pipe issues, which conveys the gas to a gasometer. When oil gas is to be obtained, the vessel *b* is filled with oil, and pieces of bricks are put into the retort *a*, the cover is then secured by a rod of iron passing through the ears *e e*, and the joint is made tight by a mixture of about 2 parts of muriate of ammonia 1 of sulphur and 30 of cast iron filings or borings, made into a paste with water.¶ This retort may be placed in any convenient furnace, and when heated to redness the cock *f* is turned so as to allow the oil to pass drop by drop. The same apparatus may be used for obtaining the gas from the oleaginous seeds, peat, &c. W.

‡ *Phil. Trans.* 1808.

§ See also *Edin. Philos. Jour.* 1825.

|| An account of the apparatus for the production of coal gas, and of its construction and expense, will be found in the *Treatises on Gas Lights*, Mr Accum and Mr Peckston.

¶ This cement should be allowed to become hard before the apparatus is used.

the shaft into the air, the mine becoming as it were an enormous piece of artillery from which they are projected; or they are gradually suffocated, and undergo a more painful death from the carbonic acid and nitrogen remaining in the mine, after the explosion of the *fire damp*; or what, though it appears the mildest, is perhaps the most severe fate, they are burned or maimed, and often rendered incapable of labour and of healthy enjoyment for life.*

Sir H. Davy has given a sketch of different, but ineffectual, contrivances of others, for the prevention of these dreadful, and hitherto frequently occurring, accidents; and has described the train of investigation by which he was led to the discovery of a remedy at once simple and efficient, and which has already been submitted to repeated and successful trials. Safety-lamp.

769. The properties of flame, and the principle of safety adopted in this lamp, have already been adverted to (200). It is obvious, from what has there been said, that if the flame of a common lamp be every where properly surrounded with a wire-gauze, and in that state immersed into an explosive gaseous mixture, it will be inadequate to its inflammation, that part only being burned which is *within* the cage, communication to the inflammable air *without* being prevented by the cooling power of the metallic tissue; so that by such a lamp the explosive mixture will be consumed, but cannot be exploded. Theory of its action.

Fig. 118 is a representation of the safety lamp, as recommended for general use by Sir H. Davy. *a* is a cylinder of wire gauze, with a double top, securely and carefully fastened, by doubling over, to the brass rim *b*, which screws on the lamp *c*. The whole is protected and rendered convenient for carrying, by the frame and ring *d*. If the cylinder be of twilled wire-gauze, the wire should be at least of the thickness of one-fortieth of an inch, and of iron or copper, and 30 in the warp, and 16 or 18 in the weft. If of plain wire gauze, the wire should not be less than one-sixtieth of an inch in thickness, and from 28 to 30 both warp and woof.†

The operation of this lamp may be shown on a small scale by suspending it in a glass jar, and then admitting a sufficient stream of coal gas to render the enclosed atmosphere explosive. The flame of the lamp first enlarges, and is then extinguished, the whole of the cage being filled with a lambent blue light; on turning off the supply of the gas this appearance gradually ceases, and the wick becomes rekindled, when the atmosphere returns to its natural state. Exp.

770. When a small coil of platinum wire is hung above the wick of the lamp within the wire gauze cylinder, the metal continues to glow, long after the lamp is extinguished, and affords light enough to guide the miner in what would otherwise be impenetrable darkness. In this case the combustion of the fire damp is continued so slowly, and at so low a temperature, as not to be adequate to that ignition of gaseous matter, which constitutes flame, though it excites a temperature sufficient to render platinum wire luminous.‡ Effect of a platinum wire.

* Davy, *on the Safety-lamp for Coal Miners*, London, 1818.

† Ibid. p. 114, *et seq.*

‡ As the *safety* of these lamps entirely depends upon the perfect state of the wire gauze, and upon the non-existence of any aperture or channel sufficiently large to admit of the passage of flame, they should, when used in a coal mine, be inspected daily to ensure their soundness in these respects.

Method of
analysing
mixtures of
carburetted
hydrogen,
&c.

771. The analysis of a mixture of hydrogen with carburetted hydrogen, carbonic oxide, and carbonic acid, presents peculiar difficulties in the ordinary mode of proceeding; and as it often requires to be performed in investigations relating to the gases used for illumination, it became an object to facilitate the process, for which Mr Brande used the following plan.

A hundred measures of the gas were introduced into a graduated tube, and the carbonic acid absorbed by a solution of potassa; the remaining gas is then transferred to thrice its volume of chlorine of known purity, standing over water in a tube of about half an inch in diameter, and exposed to daylight, but carefully excluded from the direct solar rays; after 24 hours the carburetted hydrogen and the excess of chlorine will have been absorbed, and the remaining gas, consisting of carbonic oxide and hydrogen, may be analyzed by detonation with oxygen in excess; the measure of carbonic acid formed being equal to that of the original carbonic oxide.

This proceeding depends upon the non-formation of chloro-carbonic (743) acid in a mixture of carbonic oxide and chlorine in the contact of water, and out of the direct agency of the solar rays. Such mixture has been kept several days, occasionally renewing the chlorine as it became absorbed by the water, and no diminution in the bulk of the carbonic oxide has been observed. In all these cases it is necessary to ascertain the purity of the chlorine by its absorption by water, and to be aware of the evolution of common air from water during that process.*

Bi-carburet
of Hydrogen.

772. When oil gas is compressed a colourless fluid is deposited, which is nearly insoluble in water, but soluble in alcohol, ether and oils. It burns with a dense flame, and is distinguished from the oil from which it originated, by not being acted upon to any extent, by solutions of alkalis. Part of this fluid is volatile at 60° , while other parts are more fixed. By repeated distillations Mr Faraday obtained from it a series of products from the most to the least volatile. These were subjected to a low temperature, and some of them concreted into a crystalline mass, and a substance was ultimately obtained, principally by pressure at low temperatures, which proved to be a new compound of carbon and hydrogen. At common temperatures it is a colourless liquid, of specific gravity 0,85 at 60° , and has the odour of oil gas. Below 42° it is a solid body forming dendritical, transparent crystals. At 0° it appears white or transparent, brittle, pulverulent, and of the hardness nearly of loaf-sugar. It evaporates entirely in the air: at 186° it boils, furnishing a vapour, which has a specific gravity of 40 nearly compared to hydrogen as 1. At a higher temperature the vapour is decomposed, depositing carbon. It is combustible, liberating charcoal, if oxygen be not abundantly present.

* For a discussion of the comparative illuminating power of oil and coal gases, see *Edin. Philos. Jour.* 1825.

773. This substance was analysed by being passed over red-hot oxide of copper, and by detonation of its vapour with oxygen, and was found to consist of

| | | | |
|---|-------------------------|-----------|-------|
| 2 | proportionals of carbon | | 12 |
| 1 | “ hydrogen | | 1 |
| | | | <hr/> |
| | | | 13 |

Analysis.

And in the state of vapour one volume was found to consist of 6 proportionals of carbon and 3 of hydrogen = 39.

It has been called by Mr Faraday *Bi-carburet of hydrogen*.

774. From the more volatile portions of the fluid Mr Faraday obtained a product, which, though gaseous at common temperatures, condensed into a liquid at 0°. It was very combustible, and constant in composition and properties. Its sp. gr. was 27 or 28 in its gaseous state; as a liquid 0,627; being the lightest substance, not a gas or vapour, known. It was found to consist of 1 proportional of carbon = 6, + 1 of hydrogen = 1, as is the case with olefiant gas; but these are so condensed and combined, as to occupy only one half the volume they do in that substance. A volume therefore of this gas contains 4 proportionals of carbon = 24 + 4 of hydrogen = 28, which is its specific gravity.

Other products.

775. Besides the remarkable difference, thus established, between this substance and olefiant gas, it is also distinguished by the action of chlorine, with which it forms a fluid body having a sweet taste, and resembling hydro-chloride of carbon; but from which a chloride of carbon cannot be obtained by the further action of chlorine and light.

776. The fluid as originally obtained when put into gas burning with a blue flame, makes it produce a bright white flame; it is an excellent solvent of caoutchouc, and will answer all the purposes to which essential oils are applied as solvents.*

777. *Carbon and Nitrogen—Carburet of Nitrogen—Cyanogen*.—This gaseous compound was discovered by Gay-Lussac in 1815,† and was called cyanogen from *χάρος*, blue, and *γεννάω*, I generate, because it is an essential ingredient of Prussian blue.

Union with Nitrogen.

To obtain cyanogen, it is necessary first to boil fine powdered red oxide of mercury with twice its weight of prussian blue and a sufficient quantity of water. The compound is perfectly neutral, and crystallizes in long four-sided prisms truncated obliquely. It still, however, contains a little iron, which may be separated by digesting the liquor, before evaporation, with a little more of the oxide of mercury, and saturating the excess of this oxide with a little prussic acid, or even with a little diluted muriatic acid. The cyanide of mercury, thus obtained neutral and crystallized, must be carefully and completely dried at a temperature below that of boiling water, and then exposed to heat in a small glass retort, or in a tube closed at one extremity. It first blackens, then liquefies, and the cyanogen comes

Process for obtaining cyanogen

* See *Philosophical Magazine*, lxvi. 73.

† *Annales de Chimie*, xcv.

over in the form of a gas, which may be collected over mercury. In the retort there remains a charry matter of the colour of soot, and as light as lamp black, derived from the cyanogen itself; a portion of which is decomposed by the temperature employed in its formation; but Gay-Lussac states that no free nitrogen is disengaged till towards the close of the process.*

Properties.

778. Cyanogen is a true gas, or permanently elastic fluid. Its smell is strong, penetrating, and disagreeable, resembling that of bitter almonds. It burns with a bluish flame mixed with purple. Its specific gravity is to that of common air as 1,8064 (1,8055, T.) to 1.† 100 cubic inches at 60° Fah. weigh 55 grains; at the temperature of 45° F., and under a pressure of 3,6 atmospheres, it was obtained by Mr Faraday as a limpid liquid, which resumed the gaseous form when the pressure was removed.‡

Absorbed by water.

779. Water at the temperature of 60° Fah. absorbs almost 4½ times its volume, and pure alcohol 23 times its volume. The watery solution reddens litmus; this, however, is scarcely to be considered as an effect of cyanogen, but of the products to which it gives rise by the decomposition of water.§ H. 1. 451.

The aqueous solution, according to Vauquelin,|| is subject to spontaneous decomposition, being gradually converted into carbonic and hydrocyanic acids, ammonia, a peculiar acid which he calls the *cyanic*, and a brown substance containing carbon; the ammonia saturates the acids, and the carbonaceous compound is deposited. These changes are referable to the mutual reaction of the elements of cyanogen upon those of water.

Analysis.

780. Cyanogen may be analyzed by detonation with oxygen. One volume, detonated over mercury with two of oxygen, produces two volumes of carbonic acid, and one of nitrogen. Whence it appears that cyanogen consists of two proportionals of carbon = 12, and 1. of nitrogen = 14, the nitrogen having suffered no change of bulk by uniting with the carbon; or it may be said to consist of two volumes of gaseous carbon + one volume of nitrogen, the three being condensed into one volume. Its representative number is 26.

The following symbols exhibit the mixture of cyanogen with oxygen in the above proportions, and the result of their detonation :

Before detonation.

One proportional of Cyanogen and four of Oxygen.

| | |
|--------------------|--------------|
| Cyanogen. C. N. | Oxygen 8. |
| 12+14 | 8. |
| | 8. |
| | 8. |

After detonation.

Two proportionals of Carbonic Acid.

| | |
|---|--------------|
| 6 | Oxygen 8. |
| | 8. |
| | 8. |
| 6 | 8. |
| | 8. |

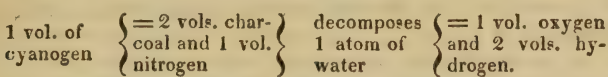
One proportional of Nitrogen.

| |
|----------------|
| Nitrogen 14 |
|----------------|

* Gay-Lussac, *Ann. de Chim.* vol. xcv. ; or Thomson's *Annals*, viii. 37. † Its specific gravity, Oxygen, = 1 is 1,625. T. ‡ For the details of the process, see Faraday's *Chemical Manipulation*, p. 417. § Vauquelin in *Ann. of Phil.* xiii. 430. || *Annales de Chim.*, Oct. 1818.

781. The solutions of pure alkalies and alkaline earths absorb cyanogen ; and the liquid obtained, when poured into a solution of black oxide of iron, affords Prussian blue, but not without the addition of an acid. At the same time, carbonic acid gas escapes, in volume equivalent to the cyanogen absorbed, and there is a perceptible smell of prussic acid. These changes will be more evident from the following recapitulation.

Absorbed by alkaline solutions, &c.



One volume of charcoal, uniting with one volume of oxygen, forms one volume of carbonic acid ; the remaining volume of charcoal, uniting with half a volume of nitrogen and half a volume of hydrogen, composes 1 volume of prussic acid ; and the residuary half volume of nitrogen and 1½ volume of hydrogen compose together one volume of ammonia. H. 1. 452.

782. Cyanogen has a remarkable tendency to combine with elementary substances, and with the metals ; but for the metallic oxides its affinity is comparatively feeble. Its compounds, which are not acid, are termed *cyanides*, or *cyanurets*.

783. *Cyanogen and Chlorine* combine and produce the *Chloro-cyanic acid*. Chloro-cyanic acid was discovered by Berthollet, who found that hydro-cyanic acid (100), by absorbing chlorine, acquires new properties, and no longer forms a blue precipitate with the solutions of iron. Supposing it to result from the union of oxygen with the prussic acid, he gave to the new compound the name of *oxy-prussic acid*. The nature of this combination has since been investigated by Gay-Lussac. To prepare it a current of chlorine gas may be passed through a solution of hydro-cyanic acid in water, till the liquid discolours a solution of indigo in sulphuric acid. By agitating this liquid with mercury, and by distilling at a gentle heat, an elastic fluid is formed. This, however, is not pure chloro-cyanic acid, for at temperatures from 60° to 70° F., and under common pressures, that acid can only exist as a liquid. It is a mixture of carbonic acid and chloro-cyanic acids. H. 1. 457.

Union of cyanogen and chlorine,

Chloro-cyanic acid,

784. M. Serullas has obtained this compound, which he terms cyanuret of chlorine, in a separate state, and perfectly pure, by the following process. Moisten cyanide of mercury with chlorine, stop the flasks, and put them in a dark place, in eight or ten hours the contents are entirely converted into perchloride of mercury and cyanide of chlorine. This compound is very deleterious, soluble in water, and still more so in alcohol : it suffers no change in these fluids, and may be separated from solution in water by passing it over chloride of calcium into bottles placed in a freezing mixture, where it becomes solid.

how obtained.

785. One of the most remarkable properties of this compound is that of crystallizing in long transparent needles at 0° F. ; and at about 20° or 25° above this it becomes liquid, or

Properties.

under a pressure of 4 atmospheres, and it remains so in tubes hermetically sealed.*

786. The chloro-cyanic acid obtained by the first process is a colourless and very volatile liquid, having a peculiar and irritating odour. It reddens litmus; is not inflammable; and does not form detonating mixtures either with oxygen or hydrogen.

Composition. 787. According to the analysis of Gay-Lussac, this acid is constituted of

| | |
|------------------------------------|----------------------------|
| 1 vol. of gaseous carbon | } condensed into 1 volume. |
| $\frac{1}{2}$ a volume of nitrogen | |
| $\frac{1}{2}$ " " " chlorine | |

In other words 1 vol. of chlorine, and 1 vol. of cyanogen produce by combining 2 vols. of chloro-cyanic acid. Hence its density should be the mean of those of its components. H. 1. 446.

The following symbols represent its composition and volume

| Cyanogen | Chlorine | Chloro-cyanic Acid. |
|----------|----------|---------------------|
| 26,0 | 36 | 62 |

Cyanogen
and Bromine.

788. *Cyanogen and Bromine* combine and form a *cyanide of bromine*, for the preparation of which the following process has been given by M. Serullas.†

Two parts of dry cyanide of mercury are to be placed in a tubulated retort, or at the bottom of a long tube, and being well cooled in a refrigerating mixture, one part of bromine is to be added; powerful action ensues, much heat is developed and a bromide of mercury with a cyanide of bromine are formed: the latter crystallizes in long needles about the middle of the tube, the small quantity of vapour of bromine gradually disappearing. A small receiver being then attached to the tube, and well cooled, the cyanide is to be sublimed into it, and will form small colourless, transparent crystals, sometimes acicular, sometimes cubical.

Properties.

This substance is very volatile, and has a penetrating odour; it becomes vapour at 60° F., and crystallizes suddenly on cooling. It is soluble in alcohol and water. It is excessively deleterious; a grain dissolved in water proved instantly fatal to a rabbit.

Cyanogen
and Iodine.

789. *Cyanogen and Iodine* form a volatile solid compound, which has an acrid taste and pungent smell; it may be prepared by heating iodine with cyanide of mercury. The following process has been recommended by M. Serullas.‡

Place a large glass jar with its mouth upon a plate of glass: mix two parts of cyanide of mercury with one part of iodine, and heat the mixture in a small porcelain capsule until the temperature being sufficiently raised, the cyanide begins to form: then quickly place it under the jar, and leave the operation to itself; the production of cyanide of iodine will continue for fifteen or twenty minutes, presenting the appearance of a multitude of snow-white flocculi, of the utmost degree of whiteness and beauty; these will gradually collect on the plate, and may be afterwards secured.

* Jour. de Pharmacie, Sept. 1827.

† Ann. de Chim. xxxiv. 95.

‡ Ann. de Chim. xxxiv. 100.

According to M. Serullas it is a compound of 1 atom of iodine + 1 cyanogen.

790. *Cyanogen and Hydrogen*—*Hydro-cyanic* or *Prussic acid*—This triple compound may be obtained by moistening cyanide of mercury with muriatic acid, and distilling at a low temperature, having surrounded the receiver with ice. Union of cyanogen and hydrogen.

791. A liquid is thus obtained which has a strong pungent odour, very like that of bitter almonds; its taste is acrid, and it is highly poisonous. When a rod dipped in the concentrated acid is brought in contact with the tongue of an animal, it expires before the rod can be withdrawn. Its vapour occasions nausea, headache and faintness.* It volatilizes so rapidly as to freeze itself. It reddens litmus.

792. The hydro-cyanic acid is used in medicine, and several formulæ have been given for its preparation; the following affords the acid of a convenient strength, and is that which is adopted at Apothecaries' Hall. (Lond.) One pound of cyanide of mercury is put into a tubulated retort with six pints of water, and one pound of muriatic acid, specific gravity 1,15; a capacious receiver is luted to the retort, and six pints are distilled over. The specific gravity of the product is 0,995.† Preparation of hydro-cyanic acid.

793. M. Vauquelin's method of preparing dilute hydro-cyanic acid, consists in passing sulphuretted hydrogen through a solution of cyanide of mercury, which, when decomposed, is to be filtered and mixed with carbonate of lead, in order to separate the excess of sulphuretted hydrogen. As this acid in its dilute state suffers partial decomposition by keeping, it should be prepared in small quantities only for pharmaceutical use, and preserved in vessels excluded from light. Vauquelin's method.

794. Hydro-cyanic acid may also be collected in a gaseous form over mercury, by heating in a retort the crystallized ferrocyanate of potassa with dilute sulphuric acid. This gas is absorbable by water and alcohol. It is speedily fatal when received into the lungs of small animals. At a temperature between 86° and 95° F., the acid gas forms with oxygen gas a mixture which detonates on passing an electric spark. A quantity equal to 100 measures condense 125 measures of oxygen, and there result 100 measures of carbonic acid and 50 measures of nitrogen. But as the carbonic acid contains only its own volume of oxygen, there remain 25 measures of the latter gas which must have been converted into water by 50 measures of hydrogen existing in the prussic acid vapour. From these and other facts, Gay-Lussac infers that it is composed of one volume Gaseous hydro-cyanic acid.

* See Bigelow's *Sequel to U. S. Pharmacopœia*, p. 49.

† The specific gravity of the acid is considered by Dr Ure as an inadequate test of its strength; and he recommends the following as a more simple method of analysis. "To 100 grains, or any other convenient quantity, of the acid, contained in a small phial, add, in succession, small quantities of the peroxide of mercury in fine powder, till it ceases to be dissolved on agitation. The weight of the oxide taken up, being divided by four, gives a quotient representing the quantity of real prussic acid present. By weighing out beforehand on a watch glass 40 or 50 grains of the peroxide, the residual weight of it shows at once the quantity expended." (*Quarterly Journal*, xiii. 312.)

of the vapour of charcoal, half a volume of hydrogen, and half a volume of nitrogen, condensed into one volume.

Composition.

795. When potassium is heated in hydro-cyanic vapour, it evolves hydrogen gas equal to half the volume of the vapour. The other elements of the gas unite with the potassium. Thus the hydro-cyanic acid is resolved into hydrogen and cyanogen, which last, uniting with the potassium, forms a cyanide of that metal. As hydro-cyanic acid is constituted of equal volumes of those two gases, united without condensation, the specific gravity of the acid gas ought to be the mean of those of its components, viz. 0,9360 very nearly. This differs very little from the result of experiments, viz. 0,9476. Its constituents, therefore, are by weight

| | |
|--------------------|-------|
| Cyanogen | 100 |
| Hydrogen | 3,846 |

or two atoms of charcoal = 12 + 1 of nitrogen = 14 + 1 of hydrogen, and its equivalent number is 27.

796. The salts formed by the union of this acid with salifiable bases are called *hydro-cyanates*, but they are not permanent, and have no useful properties. They are decomposed by the weakest acids, such as the carbonic. H. 1. 455.

Oxy-cyanic,
or cyanic
acid,

797. *Oxy-cyanic*, or *Cyanic Acid*.—This acid was first obtained in a state of combination, by M. Wöhler, by causing a watery solution of baryta, at the bottom of which were undissolved crystals of that earth, to absorb cyanogen. The barytic salt was decomposed by mixing its solution with one of an alkaline sulphate.* He now obtains the cyanate of potassa directly, and in great abundance, by the following process: Calcine, at a low red heat, (for a strong heat destroys the cyanic acid) equal weights of anhydrous ferro-cyanate of potassa and peroxide of manganese. Pulverize the remaining mass, and boil it with alcohol 86 per cent. pure; on cooling, the salt separates in small plates resembling the chlorate of potassa.†

United to
bases.

798. The acid, thus obtained in combination with potassa, may be transferred by double decomposition to other bases; but it has not yet been exhibited in a separate state. To this the easy disunion of its elements by other chemical agents, and even by an increased temperature, is a powerful obstacle. When cyanate of potassa in solution is merely heated, the cyanic acid is decomposed, and carbonic acid and ammonia are generated; and still more readily if a weak acid be added. This property served as the ground work of a method of analysis, by which Wöhler determined cyanic acid to consist of

Composition.

| | |
|--------------------------|----|
| Carbon 2 atoms | 12 |
| Nitrogen 1 ——— | 14 |
| Oxygen 1 ——— | 8 |

Weight of its atom 34

| | |
|---------------------------------|----|
| Or of Cyanogen 1 atom | 26 |
| Oxygen 1 ——— | 8 |

Weight of its atom 34

* *Quart. Jour.* xiv. 422. xvi. 104.

† *Ann. de Chem. et de Phys.* xxvii. 196.

799. It is remarkable that the above is precisely the constitution assigned by Liebig and Gay-Lussac to cyanic acid as it exists in a class of salts, to which they have given the name of fulminates. These salts owe their detonating properties to a peculiar acid, which is formed by the action of silver or mercury on nitric acid and alcohol, and which may be transferred from the oxides of those metals to other bases. Potassa for instance, digested with fulminating silver, forms a crystallizable and detonating fulminate. In all salts of this kind, the elements of cyanic acid exist, constituting with a metallic oxide, which may differ in different cases, the acid that gives to each salt its peculiar properties. Beside the metallic oxide, entering as an element into the fulminic acid, the fulminating salt contains another portion either of the same or of a different oxide which serves as a base. The fulminic acid has not, however, any more than the cyanic, been obtained separate; for when this was attempted either the fulminates were not decomposed by the acids added with that view, or the fulminic acid was resolved into its constituent principles, which, with the elements of the decomposing acid, formed new compounds. When muriatic acid, for instance, was made to act on fulminate of silver, an acid compound was formed of chlorine, carbon and nitrogen, which, among other peculiar properties, had that of changing the colour of per-chloride of iron to a deep red.* H. 1. 456.

Fulminic acid.

* 800. *Sulpho-cyanic Acid*.—This acid was discovered in 1808 by Mr Porrett, who ascertained that it is a compound of sulphur, carbon, hydrogen and nitrogen, and described it under the name of *sulphuretted chyazic acid*.† It is now more commonly called sulpho-cyanic acid, and its salts are termed sulphocyanates.

Sulpho-cyanic acid,

801. This acid is obtained by mixing so much sulphuric acid with a concentrated solution of the sulpho-cyanate of potassa as is sufficient to neutralize the alkali; and then distilling the mixture; an acid liquor collects in the receiver, which is sulpho-cyanic acid dissolved in water, and the sulphate of potassa remains in the retort.

how obtained.

802. As thus prepared it is a transparent liquid, which is either colourless or has a slight shade of pink. Its odour is somewhat similar to that of vinegar. The strongest solution of it which Mr Porrett could obtain had a specific gravity of 1.022. It boils at $216^{\circ} 5$ F.; and at $54^{\circ} 5$ F. crystallizes in six sided prisms. It reddens litmus paper and forms neutral compounds with alkalies.

Properties.

803. Its presence, is easily detected by a per-salt of iron, with the oxide of which it unites, forming a soluble salt of a deep blood red colour. With the protoxide of copper it yields a white salt, which is insoluble in water.

Test.

* *Ann. de Chim. et de Phys.* xxiv. 294. xxv. 285.

† The term chyazic being compounded of the first letter of carbon, the first syllable of hydrogen and azote, with the usual termination signifying an acid.

804. According to the analysis of Mr Porrett* which is confirmed by that of Berzelius,† the sulpho-cyanic acid is composed of

* Composition.

| | | | |
|----------|-----------|----|-----------|
| Cyanogen | | 26 | or 1 atom |
| Sulphur | | 32 | " 2 atoms |
| Hydrogen | | 1 | " 1 atom |

Or of

| | | |
|-------------------------|----|-----------|
| Bisulphuret of cyanogen | 53 | or 1 atom |
| Hydrogen | 1 | " 1 " |

Ferro-cyanic acid.

Processes for obtaining.

805. *Ferro-cyanic Acid*.—The ferro-cyanic acid has, within these few years, been the subject of able researches by Mr Porrett,‡ Berzelius,§ and M. Robiquet.¶ Mr Porrett recommends two methods for obtaining the ferro-cyanic acid, by one of which it is procured in crystals, and by the other in a state of solution. The first process, consists in dissolving 58 grains of crystallized tartaric acid in alcohol, and mixing the liquid with 50 grains of the ferro-cyanate of potassa dissolved in the smallest possible quantity of hot water. The bi-tartrate of potassa is precipitated, and the clear solution, on being allowed to evaporate spontaneously, gradually deposits ferro-cyanic acid in the form of small cubic crystals of a yellow colour.

In the second process, the ferro-cyanate of baryta, dissolved in water, is mixed with a quantity of sulphuric acid, which is precisely sufficient for combining with the baryta. The insoluble sulphate of baryta subsides, and the ferro-cyanic acid remains in solution. According to Mr Porrett, every ten grains of the ferro-cyanate of baryta require so much liquid sulphuric acid as is equivalent to 2.53 grains of real acid.

Properties.

806. The ferro-cyanic acid is neither volatile nor poisonous in small quantities, and has no odour. It is gradually decomposed by exposure to the light, forming hydro-cyanic acid and Prussian blue; but it is far less liable to spontaneous decomposition than the hydro-cyanic acid. It differs also from this acid by possessing the properties of acidity in a much greater degree.

Opinions as to its nature.

807. Different opinions have prevailed as to the nature of this acid. Berzelius maintains that it is a super-hydrocyanate of the protoxide of iron; but M. Robiquet has shown that this supposition is inconsistent with the phenomena. The view which is now commonly taken of the composition of this acid was suggested by Mr Porrett. On exposing the ferro-cyanate of soda to the agency of galvanism, the soda was observed to collect at the negative pole, while oxide of iron, together with the elements of hydrocyanic acid, appeared at the positive. From this he inferred that the iron does not act the part of a base in the salt, but that it enters into the constitution of the acid itself. Mr Porrett at first considered the iron to be in the state of an oxide; but he concludes from subsequent researches, that the ferro-cyanic acid contains no oxygen, and that its sole elements

* *Ann. of Philos.* xiii.

† *Ann. de Chim. et de Phys.* xvi.

‡ *Phil. Trans.* 1814 and 1815. *Ann. of Philos.* xiv.

§ *Ann. de Chim. et de Phys.* xv.

¶ *Ibid.* xvii.

are carbon, hydrogen, nitrogen and metallic iron. To the acid thus constituted, he proposed the name of *ferruretted chyzic acid*; but the term *ferro-cyanic* introduced by the French chemists, is more generally employed. T.

This view explains why the iron in triple prussiates (ferrocyanates) is not discoverable by the most delicate tests, for it can no more be affected by them, than sulphur can be indicated by its appropriate tests when existing in sulphuric acid.

808. According to the latest analysis by Mr Porrett, ferro-cyanic acid consists of 1 atom of hydro-cyanic acid + 2 atoms of charcoal + 1 atom of metallic iron. M. Robiquet, on the other hand, regards it as compounded of the elements of hydro-cyanic acid and of *cyanide* of iron, in the same manner as we may conceive alcohol to be formed of water and olefiant gas.* The result of his researches, together with the analysis of Berzelius, appears to justify the conclusion that the ferro-cyanic acid is composed of

| | | |
|-------|-------------------|---------|
| Or of | Hydrogen . . . | 2 atoms |
| | Iron | 1 atom |
| | Cyanogen . . . | 3 atoms |
| | Hydro-cyanic acid | 2 atoms |
| | Cyanide of iron | 1 atom |

809. The ferro-cyanic acid is, therefore, analogous to several acids, such as the muriatic, hydriodic, and hydrosulphuric acids, all of which contain hydrogen as an essential element, and which for this reason are termed *hydracids*. Under this view, the ferro-cyanic acid may be regarded as a compound of a certain *radical* and hydrogen.

810. The salts of ferro-cyanic acid were once called *triple prussiates*, on the supposition that they are composed of prussic or hydro-cyanic acid, in combination with the oxide of iron and some other alkaline base. They are now termed *ferrocyanates*.†

811. *Carbon and Sulphur—Bi-sulphuret of Carbon.*—This substance was discovered in 1796 by Lampadius who regarded it as a compound of sulphur and hydrogen, and termed it *alcohol of sulphur*. Clement and Desormes first declared it to be a sulphuret of carbon, and their statement was confirmed by Berzelius and Dr Marcet.‡

812. It may be obtained by heating in close vessels the native bi-sulphuret of iron (iron pyrites) with one fifth of its weight of well dried charcoal, or by passing the vapour of sulphur over fragments of charcoal heated to redness in a tube of porcelain.§

* *Ann. de Chim. et de Phys.* xvii. 197.

† See Henry and Turner, p. 463—315.

‡ *Phil. Trans.* 1813.

§ A coated earthen tube, of about one inch and a half in diameter, partly filled with small pieces of charcoal, well prepared and quite free from moisture, may be disposed in a furnace, as represented g. 119, one end being placed higher than the other. To this end may be adapted a glass tube, open at both ends, containing small bits of sulphur; and to the other end, by means of an adapter, is to

Process for preparing.

Pl. v.

Properties.

813. The bi-sulphuret of carbon has the following properties. It is eminently transparent, and perfectly colourless. Sometimes, immediately after distillation, the oily liquid appears a little opaque and milky; but the next day it is found to have become completely limpid. It has an acrid, pungent, and somewhat aromatic taste; its smell is nauseous and fetid, though differing from that of sulphuretted hydrogen. It is insoluble in water, but soluble in alcohol and ether; its refractive power in regard to light is very considerable. Its specific gravity is 1,272. It boils at 106° , and does not freeze at -60° . It is very volatile, and the cold which it produces during evaporation is so intense, that by exposing a thermometer bulb, covered with fine lint, moistened with it, in the receiver of an air-pump, the temperature sunk, after exhaustion to -80° . When a mercurial thermometer was used, the metal froze. It has been found by Mr Murray, that when a few drops of this liquid are poured on the surface of a glass of water, the temperature of which is 32° Fahr. plumose branches of ice dart from the sulphuret to the bottom of the vessel, and the whole water is suddenly frozen. At the same time, the sulphuret becomes volatilized; and the spiculæ of ice beautifully exhibit the colours of the solar spectrum.* H. 1. 454.

Inflammable.

814. Bi-sulphuret of carbon is inflammable, and when burned with oxygen, produces sulphurous and carbonic acids.

Decomposition.

815. When transmitted over ignited copper or iron turnings, it is decomposed, the metal combining both with charcoal and sulphur; and a rose coloured fluid is obtained, differing in its sensible qualities from the original liquid, and apparently consisting of the same elements in different proportions. It is decomposed also when brought into contact with ignited peroxide of iron. H. 1. 468.

Composition.

816. The proportions of the elements of bi-sulphuret of carbon are deduced by Berthollet, Thenard, and Vauquelin, to be from 14 to 15 parts of charcoal, and from 85 to 86 of sulphur, in 100. This statement of its composition nearly agrees with that determined by Berzelius and Dr Marcet; viz.

| | | | |
|-------------------|-------|----------------|--------|
| Sulphur | 84,83 | . . . or . . . | 100, |
| Carbon | 15,17 | | 17,89 |
| | 100 | | 117,89 |

be fixed a curved tube, passed into water contained in a two-necked bottle. The part of the tube, containing the charcoal, may then be made red hot; and, when this happens, the bits of sulphur are to be pushed forwards, one by one, by means of a wire, carefully excluding the air. As soon as the sulphur comes into contact with the charcoal, bubbles of gas will be produced in great abundance, and a vapour will appear, which will condense under the water in the bottle, into a liquid, of which, in the course of a day, about half a pint may be procured. This liquid may be purified by re-distilling it at a very gentle heat, not exceeding 100° or 110° Fahrenheit; and some dry chloride of calcium may be put into the retort, in order to obtain the fluid perfectly free from water. The liquid which comes over is quite pure, and some sulphur remains in the retort.

* *Ann. of Philos.* iii. N. S.

The above-mentioned numbers establish the proportion of the elements of this compound to be two atoms of sulphur = 32 to one of carbon = 6, and its equivalent number to be 33.

817. *Phosphuret of Carbon*.—To obtain this compound Dr Thomson directs the following process.* Allow phosphuret of lime to remain in water, till it no longer evolves gas; then add to the liquid excess of muriatic acid, agitate, and filter. Phosphuret of carbon remains, which is to be washed and dried. It is a soft powder, and when exposed to the air it slowly imbibes moisture, and acquires an acid flavour. It burns at a red heat, giving out its phosphorus, the charcoal being prevented burning by a coating of phosphoric acid.

Carbon and Phosphorus.

It consists of phosphorus 0.62 + carbon 0.38.†

818. *Bi-sulphuret of Carbon and Hydrogen—Hydroxanthic or Carbo-sulphuric Acid*.—Prof. Zeise of Copenhagen, has discovered that when the bi-sulphuret of carbon is agitated with a solution of pure potassa in strong alcohol, the alkaline properties of the potassa disappear entirely; and on exposing the solution to a temperature of 32° F. numerous acicular crystals are deposited. Prof. Zeise attributes these phenomena to the formation of a new acid, the elements of which are derived, in his opinion, partly from the alcohol, and partly from the bi-sulphuret of carbon. He regards the acid as a compound of carbon, sulphur, and hydrogen. To the radical of this acid he applies the term *Xanthogen* (from *ξανθος* yellow, and *γενναω* I generate) expressive of the fact that its combinations with several metals have a yellow colour. The acid itself is called *hydroxanthic*, and its salts *hydroxanthates*. The crystals deposited from the alcoholic solution are the hydroxanthate of potassa.

Hydroxanthic acid.

819. The action of ammonia on the alcoholic solution of bi-sulphuret of carbon is very different from that of potassa. No hydroxanthate is formed; but two new salts are produced, the one containing a new acid which may be considered as a compound of sulpho-cyanic acid and sulphuretted hydrogen; the other as containing a double sulphuret of hydrogen and carbon. By this action, the ammonia and the bi-sulphuret both undergo decomposition.

Action of ammonia.

820. When a mixture of 15 to 17 measures of bi-sulphuret of carbon, 45 of alcohol, and 100 of alcohol saturated with ammonia, are put into a flask which they nearly fill, and which is then closed with a glass stopper, the mixture left at a temperature from 53° to 57° F., in about ten minutes becomes yellow, and in about twenty minutes brown. Shortly after, a great number of small feathery crystals are perceived, the greater part of which fall to the bottom of the vessel. A flocculent matter also attaches itself to the stopper, and to the parts of the glass which are not covered with liquid, of the same nature as

* System, i. 276.

† Ann. of Philos. viii. 157.

the crystals. This goes on for about an hour or an hour and a half, after which a crystallization of another kind begins; the crystals are more distinctly grouped, often in stars, have more brilliancy, and a distinct prismatic form; they continue to be deposited during 30 or 40 hours, and to increase in size, sometimes to that of half an inch. At the same time the first crop of crystals diminishes in quantity, and sometimes almost disappears. The salt first deposited is a double sulphuret of carbon and hydrogen united with ammonia. It was called the *reddening salt*, from its property of becoming speedily red by contact with the air, chiefly from the absorption of moisture. This change takes place with such facility, that it is scarcely possible to obtain it otherwise than red, unless the alcohol be removed by washing it with ether, and then by compression in bibulous paper, it may be dried, and will bear exposure to the air for five or six minutes without alteration. It dissolves entirely and readily in water, producing a brown-red solution, from which sulphuric, or muriatic acid liberates sulphuretted hydrogen. This solution gives a red precipitate with salts of lead, brown with salts of copper, and yellow with those of mercury. All these precipitates change gradually even when secluded from air; sulphuret of carbon separating, and a metallic sulphuret being left.

The second set of crystals may be obtained apart from the first, by pouring off the liquid as soon as they begin to appear, which is generally in about two hours; filtering it rapidly through paper moistened with alcohol; and leaving it in a closed wide mouthed flask for ten hours, at a temperature of 50° Fahr. In 30 hours, the liquor may be decanted, the crystals washed with a small quantity of alcohol, and the salt compressed between folds of paper. If intended to be preserved, it may be dried by keeping it, along with sulphuric acid *in vacuo*. It is nearly without odour, unless it has been exposed to a damp atmosphere; dissolves abundantly in water, but less readily in alcohol; its solution effervesces with those acids only which decompose it, such as the nitric; it is not precipitated by salts with base of lime or baryta, but is precipitated of various colours by metallic salts. Solution of potassa, heated with the yellow precipitate thrown down by per-salts of copper is neutralized, and the hydro-sulpho-cyanate of potassa of Porrett is obtained. From the analysis of this yellow precipitate, M. Zeise infers the ammoniacal salt to which he gives the name of *Hydro-sulphuretted hydro-sulphocyanate of ammonia*, to consist of one atom of ammonia, one atom of hydro-sulphocyanic acid, with two atoms of hydrogen and one sulphur.

Action of per-salts of iron.

§21. By the action of per-sulphate or permuriate of iron, added in small portions to a very dilute solution of the ammoniacal salt acidulated with muriatic acid, a snow white crystalline solid is obtained in the form of shining scales, having scarcely any odour, and not changing remarkably by contact with air.

This appears to be a *crystallized hydro-sulphuret of cyanogen*, and is probably a compound of one atom of nitrogen, two of carbon, four sulphur, and four of hydrogen.* H. 1. 472.

SECTION VI. Boron.

822. Boron was first obtained by Sir H. Davy in 1808, by the action of Voltaic electricity on boracic acid. When that acid slightly moistened with water, was exposed between two surfaces of platinum to a battery of 500 pairs of plates, an olive brown matter began immediately to appear on the negative surface, and gradually increased in quantity. This substance was found not to be acted on by water, but to dissolve with effervescence in warm nitric acid. When heated to redness on platinum, it burned slowly, and boracic acid was regenerated. Hence the name of *boron* has been applied to it. H. 1. 355.

How discovered.

823. This substance is also obtained by heating in a copper tube two parts of the metal potassium, with one of boracic acid previously fused and powdered. In this experiment the boracic acid, which consists of boron and oxygen, is decomposed by the potassium. The fused matter is washed out of the tube, and the whole put upon a filter. The boron remains in the form of a brown, insipid, insoluble powder, unaltered by exposure to air at common temperatures, but when heated to 600° it burns with much brilliancy, especially in oxygen gas, and produces *boracic acid*. It is a non-conductor of electricity. Berzelius finds the easiest and most economical method of obtaining boron, is by the decomposition of an alkaline borofluate by potassium. The boron must be washed with a solution of sal ammoniac, and finely with alcohol, because, when pure water is used, a considerable portion passes in a dissolved state through the filter.

Mode of obtaining.

824. *Boracic acid* is usually obtained by dissolving the salt called *borax* in hot water, and subsequently adding half its weight of sulphuric acid; as the solution cools, white scaly crystals appear, which, when washed with cold water are nearly tasteless, and which consist of boracic acid combined with water and retaining a little sulphuric acid, which it loses by exposure to a strong red heat, and fuses into a glass.

Boron with oxygen.

825. Boracic acid is very difficultly soluble in water; the solution reddens vegetable blues, but possesses the singular property of rendering the yellow of turmeric brown, in the manner of an alkali. Its solution in spirit of wine burns with a green flame. Its specific gravity is 1,479. This acid was first obtained by Homberg, in 1702, and was used in medicine, under the name

Properties.

* See the original memoirs in the *Ann. de Chim. et de Phys.* xxvi. 66. 113, and to an abstract in the *Quart. Jour.* xviii. 149.

of *Homborg's Sedative Salt*. Its nature was first shown by Davy.

Composition. 826. From a review of the experiments of others and researches of his own, Dr Thomson concludes that one of boron unites with two of oxygen to form boracic acid.* If, therefore, we consider it as consisting of 1 proportional of boron and 2 of oxygen, the number representing boron will be 8, and boracic acid will consist of

| | |
|----------|----|
| 1 Boron | 8 |
| 2 Oxygen | 16 |

Boracic acid 24

Crystallized boracic acid, according to the same chemist, is composed of

| | | |
|--------------|-----------|----|
| Boracic acid | . . . | 24 |
| Water | | 18 |

and its atomic weight is 42

Boracic acid is a constituent of some minerals as datholite and boracite.

Native. 827. *Native boracic acid* has been found in the Lipari islands, and also in the hot springs of Sasso, in the Florentine territory; hence the term *Sassolin* applied to it by some mineralogists.

Boron and chlorine. 828. Boron burns in chlorine gas with considerable splendour. The chloride of boron, according to M. Dumas,† may be prepared by passing dry chlorine gas over a mixture of charcoal and boracic acid, heated to incandescence in a porcelain tube. The tube should first be heated to expel all moisture from the mixture, and the gas having been passed over it for about a quarter of an hour, an adapter and bent tube are to be attached and the chloride received over mercury. It is gaseous, colourless, denser than air, fuming in contact with it, decomposable by water, and resists a high temperature.‡

Boron and Fluorine. Fluo-boric acid. 829. When perfectly dry boracic acid and fluat of lime (fluoride of calcium) were exposed to a strong heat in an iron tube, in the proportion of one part of the former to two of the latter, a gas was obtained by Gay-Lussac and Thenard, to which the name of *gas fluo-borique* or fluo-boric acid gas was given. It may also be obtained by heating in a retort twelve parts of sulphuric acid, with a mixture of one part of fused boracic acid, and two of fluor spar, reduced to a very fine powder.§ The gas must be received over mercury.

830. Fluo-boric acid gas is colourless, has a penetrating odour, and extinguishes flame. It reddens litmus paper, and forms salts with alkalies which are called *fluo-borates*.

831. It has a remarkable affinity for water. When it is mixed with air or any gas which contains watery vapour, a

* Thomson's *System*, vol i. p. 249, 5th edit.

† *Ann. de Chim.* xxx. 378.

‡ See also a process by M. Despretz, *Quart. Jour.* N. S. i. 234.

§ Dr J. Davy, *Phil. Trans.* 1812.

dense white cloud appears, which is a combination of water and fluo-boric acid gas. According to Dr Davy water absorbs 700 times its volume of this gas, caloric is evolved and the water acquires an increase of volume. The saturated solution is limpid, fuming, and very caustic.

832. Fluo-boric acid gas does not act on glass, but attacks animal and vegetable matters with great energy, converting them, like sulphuric acid, into a carbonaceous substance.

833. When potassium is heated in fluo-boric acid gas it inflames, and a chocolate-coloured solid, is produced. On putting this substance into water, a part of it dissolves, and a solution is obtained, which has all the characters of the fluat of potassa. The insoluble matter is boron. From this and other experiments it has been inferred that fluo-boric acid gas is a compound of fluorine and boron, and ascribes the combustion of potassium in it to the combination of that metal with fluorine.

Action of potassium.

834. The specific gravity of this gas was found by Dr Davy to be 2,3709 and by Dr Thomson 2,3622.

Specific gravity.

835. It appears from the experiments of Dr J. Davy* that fluo-boric acid gas is capable of condensing successively one, two and three volumes of ammonia. The first is a white solid, volatile in close vessels by a gentle heat. The two other compounds are liquid, and when exposed to the atmosphere, lose ammonia and pass into the first.

From an analysis of the second compound, Dr Thomson deduces the atomic weight of fluo-boric acid to be 34.

Composition.

According to Berzelius it is constituted of

| | |
|------------------------|-----------|
| Fluoric acid | 47,942 |
| Boracic acid | 52,058 |
| | <hr/> |
| | 100,000.† |

836. Boron takes fire and burns, when strongly ignited in the vapour of sulphur. The sulphuret is a white opaque substance, which when put into water is converted into sulphuretted hydrogen and boracic acid.

Sulphuret of boron.

SECTION VII. Silicon.

837. That silica or siliceous earth is composed of a combustible body united with oxygen, was demonstrated by Sir H. Davy; for on bringing the vapour of potassium in contact with pure silica heated to whiteness, a compound of silica and potassa resulted, through which was diffused the inflammable base of silica in the form of black particles like plumbago. To this substance,

Silicon discovered.

* Phil. Trans. 1812.

† Ann. of Philos. N. S. x. 127.

on the supposition of its being a metal, the term *silicium* was applied. But as it offered a closer analogy with boron and carbon than with the metals, Sir H. Davy and Dr Thomson gave it the name *silicon*.

Berzelius's
process.

838. Silicon was obtained by Berzelius by the action of potassium on fluosilicic acid gas.* The most convenient method of preparing it is by heating potassium with the dry fluato of silica and potassa. The residue, after being well washed with hot water, is heated to redness to expel a little hydrogen which was united to the silicon, and it is then digested in dilute fluoric acid, with the view of dissolving adherent particles of silica.

Characters.

839. Obtained in this manner silicon has a dark nut brown colour, without the least trace of metallic lustre. It is a non-conductor of electricity; incombustible in air and in oxygen gas; and may be exposed to the flame of the blow pipe without fusing or undergoing any other change. It is not acted upon by sulphuric, nitric, muriatic or fluoric acids; but a mixture of the nitric and fluoric acids dissolves it readily even in the cold.

Action of
chlorate of
potassa, &c.

840. Silicon is not changed by ignition with chlorate of potassa. In nitre it does not deflagrate until the temperature is raised so high that the acid is decomposed. With carbonate of potassa or soda it burns vividly. It explodes, in consequence of a copious evolution of hydrogen, when it is dropped upon the fused hydrates of potassa, soda, or baryta.

Silica.

Silica abund-
ant in na-
ture.

841. From synthetical experiments 48 parts unite with 52 of oxygen; supposing the elements of silica to be in equal weights, the same number, 8, would represent silicon and oxygen.

842. *Oxide of Silicon, Silica, or Siliceous Earth*, is a very abundant natural product. It constitutes a principal ingredient of several rocks, that form extensive mountain masses; it composes a large proportion of the sand found in the beds of rivers, and on the sea shore, and enters largely into several minerals, as quartz, calcedony, opal, &c. It constitutes an essential ingredient of fertile soils, and renders them porous and open to the transmission of moisture. It exists pure in rock-crystal, and nearly pure in flint, and it may be obtained tolerably pure from flints by the following process:

How obtain-
ed.

Procure some common gun-flints, and calcine them in a crucible in a low red heat. By this treatment they will become brittle, and easily reducible to powder. Mix them, when pulverized, with three or four times their weight of carbonate of potassa, and let the mixture be fused in a strong red heat, in a crucible. The materials must bear only a small proportion to the capacity of the crucible; and the heat must at first be very moderate, and slowly increased. Even with this precaution, the mass on entering into fusion, will be apt to overflow; and must be pressed down, as it rises, by an iron rod. When this

* *Ann. de Chim. et Phys.* xxvii. 337; and *Boston Jour. of Philos.* iii. 37.

effervescence has ceased, let the heat be considerably raised, so that the materials may be in perfect fusion during half an hour, and pour the melted mass on a copper or iron dish. We shall thus obtain a compound of alkali and siliceous earth. Dissolve this in water, filter the solution, and pour it into diluted sulphuric or muriatic acid. An immediate precipitation will ensue, and as long as this continues, add fresh portions of the solution. In precipitating the alkaline solution of silica, more acid must be used than is sufficient to engage the alkali; and the alkaline liquor must be added to the acid, and not the reverse; for, in the latter case the precipitate will be glass and not silica. Let the precipitate subside, pour off the liquor that floats above it, and wash the sediment with hot water, till it comes off tasteless. Then dry it.

843. Silica, obtained by this process, though pure enough for many experiments, may still contain a portion of alumina. To separate the latter earth, boil the precipitate with diluted sulphuric acid, to which a little sulphate of potassa may be added. The alumina will thus be dissolved; and the silica may be freed from the solution of alum by repeated washings with water. Even silica, however, that has been most carefully washed, still gives traces of potassa on the application of electro-chemical powers.* H. 1. 643. Separation of alumina.

According to Prof. Brande silica may be obtained of sufficient purity for most purposes by heating rock crystal to redness, quenching it in water, and then reducing it to fine powder.

844. Silica is white; its specific gravity is 2,66. It fuses at a very high temperature. In its ordinary state it is insoluble in water; but it dissolves in very minute portions in that fluid, when recently precipitated in the form of gelatinous hydrate; and in the same state it dissolves sparingly in the acids. It readily unites with the fixed alkalies, and forms *glass*; or, if the alkali be in excess, a liquid solution of the earth may be obtained (*liquor silicum*,) from which it is precipitated in the state of a *gelatinous hydrate* by acids. This alkaline solution, after having been kept for several years, has formed small crystals of silica. It sometimes forms a deposit much like calcedony, and as hard.† Properties:

845. In consequence of its possessing a stronger affinity for alkalies and earths than for acids, as well as from its other habits, silica has been thought to present a closer analogy with acids than with earths; and has been called *silicic acid* and its compounds *silicates*; but on the other hand it is deficient in some of the characters which have hitherto been deemed essential to acidity. H. 1. 645. Silicic acid.

346. *Glass* is essentially a compound of silica with fixed alkali, a variety of other substances being occasionally added for Glass.

* Davy.

† See Thomson's *First Prin.* i. 194.

particular purposes, among which oxide of lead is perhaps the most important. *Bottle glass* is obtained from a mixture of alkali and common sand, but *flint glass* is prepared from a very pure siliceous sand, a little of the oxide of lead and of manganese, being added to aid the vitrification, and prevent the green tint which is produced when any oxide of iron is present. The art of colouring glass and of making *artificial gems* is of an old date, and effected by metallic oxides.*

Annealing.

847. Glass vessels must be cooled very slowly, otherwise they become very brittle, and this process is termed the *annealing* of glass. When glass is properly prepared, very few chemical agents have any action on it. Fluoric acid, however, dissolves it readily, from the powerful affinity which it has for silica. The alkaline metals appear to decompose glass, combining with the oxygen of the potassa or silica; and Sir H. Davy found that the oxide of lead, which fine glass contains, is acted on by muriatic acid at a high temperature, chloride of lead and water being formed.†

Silicated fluor-
oric acid.

848. The only acid body which acts energetically upon silica is the hydrofluoric acid, (see *Fluate of lime*.) The result of this action is a gaseous compound, which has been called *silicated fluoric acid*, or *fluo-silicic acid*; it is probably a compound of silicon and fluorine; Berzelius maintains that it is not an acid, but a real gaseous salt, the fluato of silica, of which fluoric acid is the acid and silica the base. He regards the fluosilicates as double salts, which are composed of the fluato of an alkali united with the fluato of silica.‡ According to Dr Thomson it is composed of 1 atom fluoric acid $10 + 1$ of silica $16 = 26$.

How obtain-
ed.

To obtain this gaseous compound, three parts of fluor spar, and one of silica finely powdered, are mixed in a retort with an equal weight of sulphuric acid. Or finely powdered fluor spar may be mixed with half its weight of pulverized glass and an equal weight of strong sulphuric acid; a gentle heat is applied, and the gas evolved is to be collected over mercury.

Properties.

849. Silicated fluoric acid is a colourless gas; its odour is acrid, much resembling muriatic acid; its taste very sour; its specific gravity 3,573§ compared with air; 100 cubic inches weigh 110,78 grains.|| It extinguishes burning bodies. It pro-

* The metals employed as colouring materials are: 1. Gold. The purple of Cassius imparts a fine ruby tint. 2. Silver. Oxide or phosphate of silver gives a yellow colour. 3. Iron. The oxides of iron produce green, yellow, and brown, depending upon the state of oxidizement and quantity. 4. Copper. The oxides of copper give a rich green; they also produce a red when mixed with a small proportion of tatar, which tends partially to reduce the oxide. 5. Antimony imparts a rich yellow. 6. Manganese. The black oxide of this metal, in large quantities, forms a black glass; in smaller quantities, various shades of purple. 7. Cobalt, in the state of oxide, gives beautiful blues of various shades; and with the yellow of antimony or lead it produces green. 8. Chrome produces fine greens and reds, depending upon the state of oxidizement.

The following are the best authorities upon the subject of coloured glasses and artificial gems:—Neri, *Art de la Verrerie*. Kunkel. Fontaineau, *Encyclopedie Methodique*, *Annales de Chim. et Phys.* xiv. 57. Aikin's *Dictionary*, Art. Glass.

† *White Enamel* is merely glass, rendered more or less milky or opaque by the addition of oxide of tin: it forms the basis of the coloured enamels, which are tinged with the metallic oxides.

‡ *Ann. de Chim. et de Phys.* xxvii.

§ 3,6111, T.

|| 110,135, T.

duces white fumes when in contact with damp air; and when exposed to water, two compounds of silica with fluoric acid are formed; the one *acid*, and dissolved in the water; the other containing excess of silica and insoluble. The dry compound contains 62 per cent. of silica; the aqueous solution only retains 55 per cent. Water dissolves 263 times its bulk of this gas.

850. When one volume of silicated fluoric acid is mixed with two of ammonia, a total condensation ensues, and a dry white salt results, which is slightly acid, deposits silica by solution in water, and, when its concentrated solution is boiled in glass vessels, powerfully corrodes them. By adding excess of ammonia the whole of the silica is precipitated, and a pure fluato of ammonia is obtained. H. Action of Ammonia,

851. If silicon is heated in a current of chlorine, it takes fire and continues to burn. If the gas contains atmospheric air, some silica remains in the form of a slight skeleton. Silicon burns equally well in chlorine, whether or not it has lost its combustibility in the air. The product condenses and presents a yellowish liquid when it contains an excess of chlorine, but which is without colour when it is freed from this excess. This liquid is very fluid; it evaporates almost instantaneously when exposed to the air, yielding white vapours, and leaving a residuum of silica. It has a very penetrating smell, which may be compared in some degree to that of cyanogen. Thrown into water, it floats on the top; it generally dissolves in it, or leaves a little silica. If the quantity of water is small, a drop, for example, on as much chloride of silicon, this envelopes it, and the silica remains in a frothy semi-transparent mass. This liquid is analogous to the combinations of the other electro-negative bodies with chlorine. of chlorine,

852. At common temperatures potassium has no action on chloride of silicon; but when heated in the vapour of the latter substance it takes fire and produces a compound of potassium and silicon. of potassium.

853. Silicon heated to a perfect red in the vapour of sulphur inflames and burns, but with less intensity than in oxygen; and the combination even does not take place with the incombustible silicon. The sulphuration is usually as incomplete as the oxidation, and a scorified mass is obtained of a dark grey colour. It sometimes happens, however, particularly when a vacuum is made in the vessels before volatilizing the sulphur, that the silicon becomes completely sulphuretted, at least in a part of its mass. It then presents an earthy white body, which, thrown into water, instantly dissolves in it with the evolution of sulphuretted hydrogen. The silicon is converted into silica which dissolves in the water; and if this is in small quantity, a solution may be obtained so much concentrated, that it solidifies after a slight evaporation, and it leaves the silica, after the desiccation, in a transparent fissured mass. Silicon imperfectly sulphuretted also decomposes water rapidly, with disengagement of hydro- Sulphuret.

Action on water.

gen, and solution of the silica in the water; and the silicon which was not combined with the sulphur becomes separated. In the air the sulphuret of silicon diffuses a very strong smell of sulphuretted hydrogen, and loses in a little time all its sulphur; but in dry air it may be preserved a long time. At a red heat, it contracts and shrivels up, yielding sulphurous acid and silica. This change, however, takes place but slowly; for when kept at a red heat for some moments, it still has the property of decomposing water.

Alloys.

854. Silicon, when once isolated, combines with the metals with much difficulty. Its remarkable affinity for platinum is known by the experiments of M. Boussingault; but it may be heated as often and as long as we choose in a platinum crucible, without any combination taking place. But if we endeavour to reduce silicium by potassium in a platinum crucible, the silicon penetrates deeply into the platinum wherever this is touched by potassium. Copper, silver, lead, and tin, heated with silicon by the blow-pipe, do not seem changed in their appearance, nor in their ductility; notwithstanding when they are treated with acids they leave a small quantity of silica.

Silicon combines with potassium at a high temperature, but without the evolution of a remarkable heat. It affords two combinations; one with excess of potassium, of a dark grey, and which dissolves completely in water; the other, with less potassium, is obtained by the reduction before stated, or by exposing the first to a very strong heat.

SECTION VIII. Selenium.

Selenium was discovered in 1818 by Berzelius in the sulphur obtained by sublimation from the iron pyrites of Fahlun in Sweden.

Sources of selenium.

In the chambers for manufacturing sulphuric acid, a reddish mass is deposited, which is principally sulphur.* This substance, in burning, gave out an odour, which induced Berzelius to suspect that it contained tellurium, but on a minute examination he discovered, instead of that metal, a body with entirely new properties, to which he has given the name of *Selenium*. The process by which it was extracted, is described in the 13th vol. of *Annals of Philosophy*, p. 403.

According to Berzelius† selenium and sulphur may be separated by the following process. When sulphuret of selenium

* It has been lately discovered by M. Stromeyer amongst the volcanic products of the Lipari islands, and the peculiar orange tint of the sulphur from those islands is supposed to proceed from its presence. See *Ann. Philos.* N. S. x. 234.—Professors Stromeyer and Hausmann have given an account of a new ore of lead containing selenium. See *Boston Jour.* ii. 597. It has also been found combined with cobalt, silver, mercury and copper.

† *Phil. Mag.* N. S. ii. 390.

is fused with carbonate of potassa, the alkali not being in excess, the fused mass, dissolved in water, leaves selenium undissolved and free from sulphur.

855. The colour of Selenium varies a good deal. When rapidly cooled, its surface has a dark brown hue, and its fracture the colour of lead. Its powder has a deep red colour, but it sticks together when pounded, and then assumes a grey colour and a smooth surface. It softens at 212° Fahr., and completely fuses at a few degrees higher. While cooling, it has a considerable degree of ductility, and may be kneaded between the fingers, and drawn out into fine threads, which have a strong metallic lustre, an imperfect degree of transparency; and are red by transmitted, but grey by reflected light. When slowly cooled it assumes a granulated fracture, and is extremely like a piece of cobalt. At a temperature nearly equal to that of boiling mercury, selenium enters into ebullition; and condenses either into opaque metallic drops, or, when a retort with a large neck is used, into flowers of a fine cinnabar colour. Its vapour has a deep yellow colour, more intense than that of chlorine, but not so deep as that of sulphur.

Properties.

856. When heated before the blow-pipe, it tinges the flame of a fine azure blue, and exhales so strong a smell of horse-radish, that a fragment, not exceeding $\frac{1}{50}$ of a grain, is sufficient to fill the air of a large apartment.

857. *Selenium and Oxygen*.—Oxide of Selenium is formed by heating Selenium in a close phial with common air, which acquires a strong smell of horse-radish. Water agitated with this air imbibes the odour of the gas, and reddens litmus feebly, but this appears to be owing to the production of a small quantity of selenic acid. Selenic oxide gas is very sparingly soluble in water, and does not impart any taste to it. It does not combine with liquid alkalies.

Oxide.

858. Selenium digested in nitric or nitro-muriatic acid till it is completely dissolved, affords on evaporation a white substance which has been considered as *selenic acid*, but which, from the late experiments of M. M. Mitscherlich and Nitzsch,* who have discovered another compound containing half as much more oxygen, is more properly *selenious acid*.

859. Selenious acid has a sour taste, and leaves a slightly burning sensation on the tongue. It is very soluble in cold water, and dissolves in almost every proportion in boiling water. A saturated solution crystallizes, when rapidly cooled, in small grains, and when slowly cooled in striated prisms. The crystals dissolve in great abundance in alcohol, and the solution, when distilled, yields a fluid having an ethereal smell.

Selenious acid.

Selenious acid is easily reduced both in the moist and the dry way. When a plate of zinc or polished iron is introduced into a solution of selenious acid mixed with muriatic acid, selenium

Properties.

* *Ann. de Chim.* xxxvi. 100,

is precipitated in the form of red, or brown, or blackish plates. It is revived, also, by sulphuretted hydrogen, and sulphurous acid gases.

860. From his investigation of this acid, Berzelius has inferred it to consist of

| | | | |
|--------------|--------------------|------------|--------|
| Composition. | Selenium | 71,261 | 100,00 |
| | Oxygen | 28,739 | 40,33 |
| | | <hr/> 100. | |

On the supposition that it is constituted of an atom of base + 2 atoms of oxygen, the equivalent number for selenium will be 40, and for selenious acid 56.

Selenic acid. 861. *Selenic acid* is prepared by fusing selenium, selenious acid, a selenite or a metallic selenuret with nitre. Selenuret of lead, being the most abundant source, has been used for this purpose, but being accompanied by sulphuret, the selenic acid is usually contaminated by sulphuric acid. The selenuret of lead is to be freed from carbonates by muriatic acid, and the residue mixed with its weight of nitrate of soda, and thrown gradually into a red hot crucible. Water then dissolves out seleniate, nitrate and nitrite of soda, no selenium remaining in the residue. The solution quickly boiled, deposits anhydrous seleniate of soda, and this being separated, by cooling, crystals of nitrate of soda are formed; these being removed, ebullition again causes more seleniate to fall down, and proceeding in this way an imperfect separation is effected. The seleniate like the sulphate of soda, is most soluble in water at 181°. To purify the salt completely, the nitrite should be changed into nitrate by nitric acid.

The selenic acid is to be separated from the solution of the seleniate of soda, by nitrate of lead: the seleniate of lead being insoluble is to be well washed, and then decomposed by a current of sulphuretted hydrogen, which has no action on the selenic acid; the solution being filtered, is to be boiled, and is then diluted selenic acid.

Properties. 862. Selenic acid is a colourless liquid, which may be heated to 536° without sensible change; above that it changes, and is rapidly resolved into oxygen and selenious acid at 554°. At 329° its specific gravity is 2,524, at 512°, it is 2,6, at 509° it is 2,625; but by that time selenious acid has been formed in it.

863. A portion of the concentrated acid from which the selenious acid had been removed, was found to consist of 84,21 selenic acid, and 15,75 water.

Action of water, &c. 864. Selenic acid has a powerful attraction for water, and evolves much heat when mixed with it. It is not decomposed by sulphuretted hydrogen. Boiled with muriatic acid it produces selenious acid and chlorine, and the mixture, like aqua-regia, will dissolve gold or platinum.

Selenic acid dissolves zinc and iron, evolving hydrogen; it dissolves copper, evolving selenious acid, and it dissolves gold, but not platinum. A solution containing selenic acid is easily

decomposed, by first boiling it with muriatic acid, and then adding sulphurous acid.

865. Selenic acid is but little inferior to sulphuric acid in its affinity for bases : seleniate of baryta is not completely decomposed by sulphuric acid.*

866. *Selenium and Chlorine*.—Selenium absorbs chlorine gas, becomes hot, and forms a brown liquid, which, by an additional quantity of chlorine, is converted into a white solid mass. It has not yet been accurately separated into its component parts. Union with chlorine.

867. *Selenium and Hydrogen*.—Selenium, like sulphur, forms a gaseous compound with hydrogen, which has distinct acid properties, and is termed *seleniuretted hydrogen*, or *hydro-selenic acid*. This gas is disengaged when muriatic acid is added to a concentrated solution of any hydro-seleniate. It may also be procured by heating the seleniuret of iron in muriatic acid. Seleniuretted hydrogen.

Berzelius obtained it by fusing together potassium and selenium, adding water to the fused mass, and pouring muriatic acid on the concentrated solution.

868. This gas is colourless. Its odour is at first similar to that of sulphuretted hydrogen ; but it afterwards produces violent effects on the organs of respiration and a painful sensation in the nose, which is followed by the loss, for a time, of the sense of smelling. It is absorbed by water, forming a colourless solution, which reddens litmus paper and gives a brown stain to the skin. Properties.

It is soon decomposed by exposure to the atmosphere, and selenium subsides. It decomposes the salts of the common metals, its hydrogen combining with their oxygen and a seleniuret of the metal is formed.

869. According to Berzelius it is composed of one atom of each of its constituents.

870. *Selenium and Sulphur*.—Sulphuret of selenium is formed when sulphuretted hydrogen gas is conducted into a solution of selenious acid. The sulphuret may also be obtained by the aid of heat, but in this way it is difficult to obtain a definite compound. Sulphuret.

871. This sulphuret is of a deep orange colour, fusible at a heat a little above 212° F. and at a higher temperature may be sublimed without change. In the open air it takes fire when heated, and sulphurous, selenious and selenic acids are produced.

872. According to Berzelius it is composed of

1 atom Selenium + $1\frac{1}{2}$ sulphur.

873. The *phosphuret of selenium* may be prepared in the same manner as the sulphuret of phosphorus (679) ; but the compound formed by fusing them together can hardly be supposed to be of a definite nature. It is very fusible, sublimes Phosphuret.

* *Ann. de Chim.* xxvi. 100.—*Quart. Jour.* N. S. iv. 472.

without change in close vessels and is inflammable. It decomposes water gradually when digested in it, giving rise to seniuretted hydrogen and one of the acids of phosphorus.*

SECTION IX. *Zirconium, Glucinum and Yttrium.*

It has been remarked (369) that the bases of Zirconia, Glucina and Yttria, although agreeing in several respects with metallic bodies, are deficient in others. For the present they may be described in connection with that class of bodies to which on further investigation, they will, probably, be found to belong.

Zirconium.

Nature of
Zirconium,

how inferred,

✕ 874. The experiments of Sir H. Davy proved zirconia, to be an oxidized body, and afforded a presumption that its base, *Zirconium*, is of a metallic nature. When potassium was brought into contact with zirconia ignited to whiteness, potassa was formed, and dark particles of a metallic aspect were diffused through the alkali. The decomposition of this earth, however, had not been effected in a satisfactory manner until the year 1824, when Berzelius succeeded in obtaining zirconium in an insulated state.

how pro-
cured.

✕ 875. Zirconium is procured by heating a mixture of potassium with the fluete of zirconia and potassa, carefully dried, in a tube of glass or iron, by means of a spirit lamp. The reduction takes place at a temperature below redness, and without emission of light. The mass is then washed with boiling water, and afterwards digested for some time in dilute muriatic acid. A small portion of hydrate of zirconia however still adheres to the zirconium.

Properties.

✕ 876. Zirconium thus obtained, is in the form of a black powder, which may be boiled in water without being oxidized, and is attacked with difficulty by the sulphuric, muriatic, or nitro-muriatic acids; but is dissolved readily, and with disengagement of hydrogen by fluoric acid.

✕ 877. Heated in the open air it takes fire at a temperature far below luminousness, burns brightly and is converted into zirconia.

✕ 878. Zirconium may be pressed out into thin shining scales of a dark grey colour, and of a lustre which may be called metallic, but its particles adhere together very feebly, and it is a non-conductor of electricity.

* *Ann. of Philos.* vol. xiv.

879. The earth *zircon*, or the *oxide of zirconium*, is found in the zircon or *jargon* of Ceylon; in the *hyacinth* and in the *eudialyte* from Greenland. Zirconium and oxygen.

Zirconia is obtained by the following process: Reduce the stone to a fine powder, having previously heated it to redness, and quenched it in water. Mix the powder with nine times its weight of pure potassa, and gradually project it into a red-hot silver crucible, and keep it in perfect fusion for two hours. When the crucible has cooled, reduce the mass to a fine powder, and boil it in distilled water. Boil the undissolved residue in muriatic acid; filter, and evaporate to dryness; re-dissolve the dry mass in distilled water, and precipitate by carbonate of soda. The carbonate of zirconia which falls may be decomposed by heat.* Mode of obtaining zirconia.

880. Zirconia is in the form of a fine white powder, which, when rubbed between the fingers, has somewhat of the harsh feel of silica. It is entirely destitute of taste or smell. Its specific gravity exceeds 4. It is insoluble in water, yet appears to have some affinity for that fluid, retaining when slowly dried after precipitation, one third its weight, and appearing like gum arabic. Properties.

It is insoluble in pure liquid alkalies; nor does it combine with them by fusion, but it is soluble in alkaline carbonates.

881. Exposed to a strong heat, zirconia fuses, assumes a light grey colour; and such hardness, on cooling, as to strike fire with steel and to scratch even rock crystal. Effect of heat,

882. It dissolves readily in acids. Its solution in muriatic acid, when sufficiently heated, becomes milk white, and runs in some measure into a jelly, especially if concentrated to a certain point by evaporation. — of acids.

883. From the muriatic solution of zirconia, oxalic acid throws down a white precipitate, which is re-dissolved by an excess of the acid. Precipitates.

It is precipitated from its acid solutions, by the neutral succinates and benzoates, in copious white bulky flocks, which are again readily dissolved by an excess of succinic acid. It is also thrown down from its solutions by tartaric acid, malic acid, and tartrate of potassa.

From a sufficiently neutral solution of zirconia, ferrocyanate of potassa throws down a greenish blue precipitate, which, on

* The following method of obtaining pure zirconia is recommended by M. M. Dubois and Silveira.† Powder the zircons very fine, mix them with two parts of pure potassa, and heat them red-hot in a silver crucible for an hour. Treat the substance obtained with distilled water, pour it on a filter, and wash the insoluble part well; it will be a compound of zirconia, silica, potassa, and oxide of iron. Dissolve it in muriatic acid, and evaporate to dryness, to separate the silica. Re-dissolve the muriates of zirconia and iron in water; and to separate the zirconia which adheres to the silica, wash it with weak muriatic acid, and add it to the solution. Filter the fluid and precipitate the zirconia and iron by pure ammonia; wash the precipitates well, and then treat the hydrates with oxalic acid, boiling them well together, that the acid may act on the iron, retaining it in solution whilst an insoluble oxalate of zirconia is formed. It is then to be filtered, and the oxalate washed, until no iron can be detected in the water that passes. The earthy oxalate is, when dry, of an opaline colour; after being well washed, it is to be decomposed by heat in a platinum crucible. Thus obtained, the zirconia is perfectly pure, but is not affected by acids: It must be re-acted on by potassa as before, and then washed until the alkali is removed. Afterwards dissolve it in muriatic acid, and precipitate by ammonia. The hydrate thrown down, when well washed, is perfectly pure, and easily soluble in acids.

† *Ann. de Chim. et Phys.* xxvi. 40.

adding muriatic acid, becomes more blue, but after some time changes to a celadon green.

Hydrosulphuret of ammonia produces, in the muriatic solution of zirconia a dark olive or blackish green precipitate in very loose flocks. This precipitate may be washed in water without changing colour; but when exposed to sunshine, it becomes white.

Composition.

884. From the results of an elaborate investigation Berzelius deduces the composition of zirconia to be

| | | | |
|---------------------|--------|----|---------|
| Zirconium | 73.686 | or | 100. |
| Oxygen | 26.314 | " | 35.697. |

Glucinum.

885. We have no knowledge of the base of glucina. When obtained, its proper denomination will be *glucinum*. The general fact of its existence is proved by igniting glucina with potassium, which is thus changed into potassa.

Properties.

886. The earth *glucina* was discovered by Vauquelin in the beryl, euclase and the emerald. It is white and insipid; its specific gravity = 2.97. It dissolves in caustic potassa and soda, and thus resembles alumina, but differs from yttria. Again it differs from alumina, but resembles yttria in being soluble in carbonate of ammonia; it is much more soluble in this solution than yttria. With the acids it forms saline compounds of a sweetish astringent taste. Hence its name from *γλυκος*, *sweet*.

887. To obtain glucina from either of the above minerals proceed as follows:

Method of obtaining glucina.

Reduce it to a fine powder, and fuse it with thrice its weight of potassa; dissolve in dilute muriatic acid; evaporate to dryness; re-dissolve in water, and precipitate by carbonate of potassa. Dissolve this precipitate in sulphuric acid and add a little sulphate of potassa, and on evaporation, crystals of alum will be obtained. These being separated, add excess of carbonate of ammonia to the residuary liquor, which will retain glucina in solution, but the alumina will be precipitated; filter, and evaporate to dryness, and apply a red heat; glucina remains.

Glucina is inferred from analogy to be a compound of 1 atom glucinum + 1 atom of oxygen.

Yttrium.

Discovery.

888. In 1794 Professor Gadolin discovered a new earth in a mineral from Ytterby in Sweden, to which Ekeberg in 1797, gave the name of *Yttria*. The mineral has since been termed *Gadolinite*. Oxide of yttrium, or yttria, may be obtained by the following process:

How to obtain Yttria.

Pulverize the mineral and boil in repeated portions of nitro-muriatic acid; evaporate nearly to dryness, dilute with water, and filter; evaporate to dryness,

ignite the residue for some hours in a close vessel, re-dissolve, and filter. To this solution add ammonia, which throws down yttria and oxide of cerium; heat the precipitate red-hot, dissolve it in nitric acid, and evaporate to dryness; dilute with 150 parts of water, and put crystals of sulphate of potassa into the liquid. The crystals gradually dissolve, and, after some hours, a white precipitate appears of oxide of cerium, the whole of which must be separated by a repetition of the process. The liquor is then to be filtered, and the addition of pure ammonia forms a precipitate of yttria, which is to be washed and heated red-hot.*

889. Yttria is insipid, white, and without action on vegetable colours. It is insoluble in water, but very retentive of it: insoluble in pure alkalies, but readily soluble in carbonated alkalies. It forms salts which have a sweetish austere taste, and which have been little examined.

Properties.

890. It is precipitated from its solutions by the oxalic acid, and by oxalate of ammonia, in a state resembling fresh precipitated muriate of silver. Prussiate of potassa throws it down in small white grains passing in a short time to pearl grey; phosphate of soda in a white gelatinous form; and infusion of galls in brown flocculi.

Precipitates.

Yttria which has been a long time exposed to the action of fire, gives out chlorine gas, when dissolved in common muriatic acid; thus manifesting one property of a metallic oxide.† H. 2. 626.

The atomic weight of yttria, as deduced by Dr Thomson from the analysis of Berzelius is 42.‡

CHAPTER IV.

SECTION I.

OF THE METALS, AND THEIR COMBINATIONS.

891. The metals constitute a numerous and important class of simple substances; many of them were diligently examined by the older chemists, who have left us valuable information concerning them; many are of more recent discovery; and the existence of several others has been demonstrated within the last twenty years.

The following appear to have a sufficient claim to be considered as distinct metals.

| | | |
|---|---------|---------------------------------------|
| 1 | Gold | } Known since the remotest antiquity. |
| 2 | Silver | |
| 3 | Copper | |
| 4 | Iron | |
| 5 | Mercury | |
| 6 | Tin | |
| 7 | Lead | |

List of metals.

* Berzelius in Thomson's *Chemistry*, vol. i. p. 357.








† Nicholson's *Journal*, xviii. 77.

‡ The substance called *thorina*, supposed by Berzelius to be a distinct earth, has recently been recognized by that chemist as the phosphate of yttria.

| | Discovered by | Date. |
|---------------|---|----------------------|
| 8 Zinc | Known to Paracelsus, who died | 1541 ⁽¹⁾ |
| 9 Bismuth | Described by Agricola | 1520 ⁽²⁾ |
| 10 Antimony | “ “ Basil Valentine 15th cent. | (3) |
| 11 Arsenic | } Brandt | 1733 ⁽⁴⁾ |
| 12 Cobalt | | |
| 13 Platinum | Wood, assay master, Jamaica | 1741 ⁽⁵⁾ |
| 14 Nickel | Cronstedt | 1751 ⁽⁶⁾ |
| 15 Manganese | Gahn and Scheele | 1774 ⁽⁷⁾ |
| 16 Tungsten | M. M. Delhuyar | 1781 ⁽⁸⁾ |
| 17 Tellurium | Muller | 1782 |
| 18 Molybdenum | Do. and Hielm | 1782 |
| 19 Uranium | Klaproth | 1789 |
| 20 Titanium | Gregor | 1781 |
| 21 Chromium | Vauquelin | 1797 ⁽⁹⁾ |
| 22 Columbium | Hatchett | 1802 ⁽¹⁰⁾ |
| 23 Palladium | } Wollaston | 1803 ⁽¹¹⁾ |
| 24 Rhodium | | |
| 25 Iridium | Descostils and Tennant | 1803 |
| 26 Osmium | Tennant | 1803 ⁽¹¹⁾ |
| 27 Cerium | Hisinger and Berzelius | 1804 ⁽¹²⁾ |
| 28 Potassium | } Sir H. Davy | 1807 |
| 29 Sodium | | |
| 30 Lithium | Arfwedson | 1818 |
| 31 Barium | } Sir H. Davy | |
| 32 Calcium | | |
| 33 Strontium | | |
| 34 Magnesium | | |
| 35 Aluminium | } | |
| 36 Cadmium | | |
| | Stromyer | 1818* |

892. Of these metals the first seven were known in very remote ages. The ancients designated them by the names of the planets, to which they were supposed to have some mysterious relation; and each was denoted by a particular symbol, representing both the metal and the planet.

Ancient symbols.

| | | |
|---------------|--------------------------------|---|
| Gold was the | Sun, and was, thus represented |  |
| Silver . . . | Moon |  |
| Mercury . . | Mercury |  |
| Copper . . . | Venus |  |
| Iron | Mars |  |
| Tin | Jupiter |  |
| Lead | Saturn |  |

Native metals.

893. The metals seldom occur in the earth in a pure, or as it is termed by mineralogists, in a *native* state; but almost always united with other substances, as in the four following classes:—

i. *Native Metals* are those which occur pure or alloyed, and have but a feeble attraction for oxygen; such as platinum, gold, silver, mercury and copper.

Combined with Electro-negative substances.

ii. *Metals combined with electro-negative substances* (263.) The compounds belonging to this class are chiefly *native*:

(1) Pliny, Lib. xxxiv. chap. 2 and 10. (2) Mentioned in the *Bermannus* of Agricola written about 1530. (3) *Currus triumphalis Antimonii*. (4) *Acta Upsal.* 1733 and 42. (5) *Phil. Trans.* vol. xliv. (6) *Stockholm Trans.* (7) Bergman's *Opuscula*, vol. ii. (8) *Memoires de Toulouse*. (9) *Annales de Chimie*, vol. xxv. (10) *Phil. Trans.* (11) *Phil. Trans.* (12) Gehlen's *Jour.* ii.
* The discovery of three new metals in the Uralian platinum has been lately announced by Prof. Osann of Dorpat. *Phil. Mag. and Ann. of Philos.* No. 2, p. 394.

metallic oxides ; there are also a few native *chlorides*, and an iodide of silver has been lately discovered.* The *fluorides*, of which there are a few, may also be regarded as belonging to this class.

iii. *Metals combined with Electro-positive, or simple acidifiable, substances* (369.) This class includes the native *metallic sulphurets*, a very numerous and important series of ores, one native *carburet* only is known, that of iron. There are no native *hydrurets*, *phosphurets*, nor *borurets*.

iv. *Metals in combination with acids—Metallic salts.* Of these the most common are the native *carbonates*, *sulphates*, and *phosphates* : there are a few native *borates* ; and a few species belonging also to this class in which the oxide is united to a *metallic acid* : such as the native *arseniates*, *chromates*, *tungstates*, and *molybdates*.

894. The metals, as a class, are characterized by a peculiar lustre and perfect opacity : they are excellent conductors of heat, and of electricity.

895. They are *also* excellent reflectors, not only of light but of caloric, and hence they are the best materials for the composition of burning mirrors. From the experiments of Mr Leslie, they appear to possess this property in the following order, the highest number denoting the greatest reflecting power.

| | | | |
|-----------------------------|-----|-------------------------------|----|
| Brass | 100 | Steel | 70 |
| Silver | 90 | Lead | 60 |
| Tinfoil | 85 | Tinfoil softened by mercury . | 50 |
| Planned-block tin | 80 | | |

In general the reflecting power was found by Mr Leslie, to be proportionate to the degree of polish and to be impaired by every thing that diminished this quality. A tin reflector for example, had its reflecting power diminished nine tenths by being rubbed with sand paper.†

896. There is the greatest difference in the specific gravity of the different metals, the heaviest and lightest solids being included in the list.

The principal metals, arranged according to their specific gravities stand as follow :

| | | | | |
|---------------------|--------|----------------------|-------|-----------------------------|
| Platinum | 21,00‡ | Nickel | 8,25 | Order of specific gravities |
| Gold | 19,30 | Cobalt | 8,00 | |
| Iridium | 18,68 | Iron | 7,78 | |
| Tungsten | 17,50 | Molybdenum | 7,40 | |
| Mercury | 13,50 | Tin | 7,30 | |
| Palladium | 11,50 | Zinc | 7,00 | |
| Lead | 11,35 | Manganese | 6,85 | |
| Rhodium | 10,65 | Antimony | 6,70 | |
| Silver | 10,50 | Tellurium | 6,10 | |
| Bismuth | 9,80 | Titanium | 5,3 | |
| Uranium | 9,00 | Cerium | 4,489 | |
| Copper | 8,90 | Sodium | 0,972 | |
| Cadmium | 8,604 | Potassium | 0,865 | |
| Arsenic | 8,35 | | | |

* *Ann de Chim.* xxix. 99. † *Leslie on Heat*, p. 98.
‡ Sp. G. of rolled masses, 17,332, Haidinger.

897. The specific gravity of solids and liquids is always expressed in numbers referring to water as = 1.*

898. Among the metals, some are *malleable*, others *brittle*.

Malleability.

Malleability, or the capacity of being extended by the hammer belongs to the following metals, in the order following :

List and order of malleable metals.

| | |
|----------|-----------|
| Gold | Lead |
| Silver | Zinc |
| Copper | Iron |
| Tin | Nickel |
| Cadmium | Palladium |
| Platinum | |

Potassium, sodium, and frozen mercury, are also malleable. Malleability is one of the most useful properties of the metals. In this quality, gold takes place of all the rest, one grain may be made to cover a surface of about 52 square inches; and the thickness of each leaf of the gold sold in books does not exceed $\frac{1}{282020}$ th part of an inch.

899. Nearly all malleable metals are also *ductile*; that is, they admit of being drawn out into wires. They are arranged according to ductility as follows :

Of ductile metals.

| | |
|----------|-----------|
| Gold | Zinc |
| Silver | Tin |
| Platinum | Lead |
| Iron | Nickel |
| Copper | Palladium |

900. Different metallic wires are possessed of different degrees of *tenacity*, by which is meant the power of supporting a weight without breaking. According to the experiments of

Method of determining specific gravity.

* To ascertain the specific gravity of solids we employ a delicate balance, so contrived as to admit of substances being attached to one of the scales by means of a horse-hair or a fine thread of silk. The absolute weight of the body thus suspended is then very carefully ascertained : it is next immersed in distilled water, of the temperature of 60°; and the beam being again brought to an equilibrium, we learn the weight lost by its immersion; or, in other words, we ascertain the weight of its bulk of pure water. We now divide the sum of its absolute weight by that of the weight which it lost in water, and the quotient is its *specific weight*, or gravity, compared with water of the temperature of 60°.

Of solids.

Suppose a substance, weighing 360 grains, to lose 60 by immersion in water, the specific gravity of that substance will be = 6; for $360 \div 60 = 6$.

Of liquids.
Pl. 1.

For ascertaining the specific gravity of liquids, we generally employ a thin phial, fig. 29, holding 1000 grains of distilled water, at the temperature of 60°. If filled with any other liquid, and weighed, we learn its specific gravity; thus we should find that it would contain 13500 grains of mercury; 1850 grains of sulphuric acid; 1420 grains of nitric acid, &c., which numbers of course represent the specific gravities of those liquids.

A bottle, however, holding 1000 grains is often inconveniently large, and a small and thin globular phial, with a piece of thermometer tube ground into it by way of stopper will be found more useful: such a phial should not weigh more than from 50 to 60 grains, and may contain between 4 and 500 grains of water. To use it, it should be accurately counterbalanced in a delicate pair of scales, and then filled with distilled water, and the stopper thrust in, the capillary opening in which allows a little to ooze out, and prevents the likelihood of bursting the phial; it is then to be wiped clean and dry, and again carefully weighed, by which the quantity of water it contains is ascertained; the water being poured out, it is next filled with the liquid whose specific gravity is required, taking care that it is of the same temperature as the water; we then weigh as before, and divide the weight by the former weight of water, the product gives the specific gravity required. Thus, suppose the phial to contain 425 grains of water at the temperature of 45°, it will be found to hold 5737.5 grains of pure mercury of the same temperature; and $5737.5 \div 425 = 13.5$ the specific gravity of mercury. Or, supposing the liquid lighter than water, such as alcohol, of which we may assume the phial to contain 350.5; then $350.5 \div 425 = 0.824$ the specific gravity of the alcohol under trial. For numerous and important details on this subject, see Faraday's *Chemical Manipulation*, sect. II, 70, &c.

Guyton Morveau, the following are the weights capable of being sustained by wires $\frac{7.87}{1000}$ ths of a line in diameter.*

| | lbs. decimal avoird. parts. | | lbs. decimal avoird. parts. | |
|-----------------------------------|--------------------------------|----------------|--------------------------------|---|
| A wire of Iron supports | 549,250 | Gold | 150,753 | Metals pos- sessing tena- city, with the power of each, |
| Copper | 302,278 | Zinc | 109,540 | |
| Platinum | 274,320 | Tin | 34,630 | |
| Silver | 187,137 | Lead | 27,21† | |

901. Some of the malleable and ductile metals have, also, a high degree of elasticity. This property fits them for being applied to the mechanical purpose of springs. Steel and iron are in this respect, superior to all other metals. Upon the properties of elasticity and hardness, appears also to depend that of *fitness for exciting sound*, for whatever renders metals harder and more elastic, increases also their sonorousness. Thus bell metal is more remarkable for those properties than either tin or copper, which are its constituents. H. 1. 462.

902. None of the pure metals are very *hard*, and some so soft as to yield to the nail. In the following table some of the metals are arranged in the order of their hardness.

| | | |
|-----------|----------|-----------------------------|
| Tungsten | Bismuth | Order of their hardness. |
| Palladium | Gold | |
| Manganese | Zinc | |
| Iron | Antimony | |
| Nickel | Cobalt | |
| Platinum | Tin | |
| Copper | Arsenic | |
| Silver | Lead | |

Potassium and sodium yield to the pressure of the fingers.

903. The *structure* or *texture* of several of the metals appears to be *crystalline*. That of iron developed by the action of solvents, has been shown by Mr Daniel to be fibrous. Bismuth, and antimony have a lamellated texture; nickel presents a fracture between fibrous and foliated; and steel is granular. Several of the metals, when melted and cooled under favourable circumstances, form regular crystals. Thus bismuth, melted in a crucible, and suffered to cool, becomes covered with a crust, and when this is pierced, and the fluid beneath allowed to flow out, the cavity is found studded with beautifully regular cubic crystals. Arsenic crystallizes in regular tetraedrons, and titanium in long slender filaments or prisms. H. 1. 480.

Such are the essential physical characters of the metals; they also resemble each other in many of their chemical properties, as the following general observations show:

904. *Action of Heat*.—The metals are all susceptible of fusion by heat, but the temperatures at which they liquefy are extremely various. Mercury is fluid at all common temperatures, and requires to be cooled to -39° before it congeals. Potassium melts at 150° , and sodium at 200° : arsenic at 360° ; tin at 450° ; lead at 600° ; zinc at 700° ; and antimony at 800° . Silver, gold, and copper require a bright cherry-red heat; iron,

* *Annales de Chimie*, lxiv.

† *Ann. de Chim.* lxxi. 182.

nickel, and cobalt, a white heat; manganese and palladium, an intense white heat; molybdenum, uranium, tungsten, and chrome, are only very imperfectly agglutinated at the highest temperatures of our furnaces; and titanium, cerium, osmium, iridium, rhodium, platinum, and columbium, require the intense heat produced by an inflamed current of oxygen and hydrogen, or that of Voltaic electricity.

Volatility.

905. At higher temperatures than that required for their fusion many of the metals are volatile, and may be distilled in close vessels. Mercury, arsenic, potassium, tellurium, and zinc, are volatile at a dull red heat. Gold and silver are converted into vapour when exposed to the intense heat of the focus of a burning lens; and several of the other metals boil and evaporate under similar circumstances. It is probable that this would happen to all of them, if raised to sufficiently high temperatures.

Action of oxygen.

906. *Action of Oxygen.*—When the metals are exposed at ordinary temperatures to the action of oxygen, or of common air, which produces analogous, though less powerful effects, they are very differently affected. If the gas be perfectly dry, very few of them suffer any change unless heated in it; they then lose their metallic characters, and form a very important series of compounds, the *metallic oxides*.

Perfect or noble metals.

907. A few of the metals resist the action of heat and air so completely, that they may be kept in fusion in an open crucible for many hours without undergoing change. This is the case with gold and silver, and a few others; hence they were called *perfect* or *noble* metals: they may, however, be oxidized by the Voltaic flame; or by passing a strong electric discharge through them, when drawn into very fine wire.

Metals absorb Oxygen.

908. Other metals readily absorb oxygen when exposed to a temperature approaching a red heat; as iron, mercury, nickel, &c.; others absorb it when in fusion, as lead, tin, antimony, &c.; others at lower, or even at common temperatures, as arsenic, manganese, sodium, potassium, &c.

Calcination.

909. The product either of the slow or rapid oxidation of a metal, when heated in the air, has an earthy aspect, and was called a *calx* by the older chemists, the process of forming it being expressed by the term *calcination*. Another method of oxidizing metals is by *deflagration*; that is by mixing them with the nitrate or chlorate of potassa, and projecting the mixture into a red-hot crucible. Most metals may be oxidized by digestion in nitric acid; and nitro-muriatic acid is an oxidizing agent of still greater power.

Their attraction for oxygen different.

910. That the metals have very different attractive powers in regard to oxygen is shown by the circumstance of one metal being frequently oxidized at the expense of another; thus the oxide of mercury, heated with metallic iron, produces metallic mercury and oxide of iron; potassium, heated with oxide of manganese, becomes oxidized, and metallic manganese is obtained.

911. Some of the oxides are decomposed by mere exposure to heat, as those of gold, mercury, &c.; others require the joint action of heat, and some body having a high attraction for oxygen, such as charcoal. Thus when oxide of lead is heated with charcoal, carbonic acid gas is evolved, and metallic lead obtained.

Oxides decomposed by heat.

912. Each metal has a certain definite quantity of oxygen with which it combines; and where the same metal unites in more than one proportion with oxygen, in the second, third, and other compounds, it is a multiple of that in the first, consistent with the law of definite proportions (74). Thus 100 parts of mercury combine with 4 of oxygen to produce the *protoxide*, and with 8 to produce the *peroxide*. Copper also forms two oxides; in the one 12,5 of oxygen are united to 100 of metal, and in the other 25.

Metals combine with definite quantities of oxygen.

913. Among the combinations of metals with oxygen, some are insoluble in water, or nearly so, and have neither taste nor smell; others are soluble and sour, constituting the *metallic acids*: others are soluble and alkaline, forming the *fixed alkalies*, and *alkaline earths*. They are of all colours, and frequently the same metal united to different proportions of oxygen produces compounds differing in colour; thus we have the *black* and *red* oxide of mercury, the *white* and the *black* oxide of manganese, &c.

Metallic-acids.

914. There is a certain state of oxidation, peculiar to the different metals, in which they are most readily acted upon by the several acids. Iron and manganese, for example, at the maximum of oxidizement, are altogether insoluble in nitric acid; but readily dissolve in it, when combined with a smaller proportion of oxygen. Even when once brought into combination with that acid, the oxide, by attracting a further quantity of oxygen from the atmosphere, or from any other source, is separated in the state of an insoluble precipitate, which, however, does not consist of pure oxide, but of the oxide, with a certain proportion of acid. This explains the change, which is produced in solutions of iron, by keeping them exposed to air. The oxides of iron and manganese, saturated with oxygen, are soluble, however, in the less oxygenated acids; for example, in the sulphurous or nitrous, which first deprive the oxide of part of its oxygen, and then dissolve the less saturated oxide. H. 1. 490.

Action of acids dependent on state of oxidation of metals.

915. *Action of Chlorine*.—There are a few of the metals which resist the action of chlorine at common temperatures, but when heated they all combine with it; some slowly, others rapidly and with intense ignition. Copper leaf, powdered antimony, arsenic, &c., burn when thrown into the gas: mercury and iron inflame when gently heated in it; silver, gold, and platinum quietly absorb it. The compounds thus formed are termed *metallic chlorides*.

Action of chlorine,

916. The metallic chlorides may be also formed, by exposing certain metals to muriatic acid gas at high temperatures. In

of muriatic acid.

this case, the muriatic acid is decomposed; its hydrogen is liberated; and its chlorine combines with the metal. Diluted muriatic acid acting on certain metals (iron for example) occasions the decomposition of water; hydrogen is evolved, and an oxide formed, which unites with the muriatic acid and constitutes a true muriate. Or if the oxide of a metal be acted upon by muriatic acid, we have also a muriate formed, which, in some cases, crystallizes as such, but in others in becoming a solid is at the same moment changed into a chloride. The oxides of barium, strontium, calcium, magnesium, aluminium, copper, and manganese all form with muriatic acid crystallized muriates, containing definite proportions of water; but the oxides of potassium and sodium, when dissolved in muriatic acid, afford muriates only so long as they continue fluid, and in crystallizing become true chlorides. Mercury, silver, and lead, form chlorides only, and not muriates. When a crystallized muriate is heated, the first effect is to expel its water of crystallization, and the next is to cause the oxygen of the oxide to unite with the hydrogen of the muriatic acid, forming water, which escapes.

917. The chlorides may be formed also by double elective affinity; thus sulphate of mercury, exposed to heat with chloride of sodium, gives chloride of mercury and sulphate of soda; the oxygen and sulphuric acid passing from the mercury to the sodium, and the chlorine from the sodium to the mercury. H. 1. 499.

Properties of
the Chlorides
various.

918. The physical and chemical properties of the chlorides are extremely various. They are nearly of all colours. Some are unchanged by heat; others undergo decomposition. Some are soluble, others insoluble, in water. Several of them decompose water, giving rise to the formation of muriatic acid, and an oxide (312); or in some cases to a muriate. The same metal often forms more than one compound with chlorine, and these compounds are designated as the oxides. Thus we have the *proto-chloride* and *perchloride* of mercury, &c.

Action of
Bromine.

919. *Action of Bromine.*—The action of bromine on the metals is analogous to that of chlorine (339). M. Balard is of opinion that the soluble *metallic bromurets* are converted, like the similar compounds of chlorine and iodine into neutral hydro-bromates; and reciprocally, that the hydro-bromates are frequently converted into bromurets in passing into the solid state.

920. All the bromurets are decomposed by chlorine with evolution of bromine, and the hydro-bromates are not only attacked by chlorine, but by all substances, such as the chloric or nitric acids, which have a strong tendency to deprive other bodies of hydrogen.*

Action of
Iodine.

921. *Action of Iodine.*—Iodine aided by heat acts upon many of the metals, and produces *metallic iodides*. Some of

* *Ann. de Chim.* 1826.

these are soluble in water without decomposition; others decompose water and produce *hydriodates*; others are insoluble. The insoluble iodides may generally be formed by adding a solution of iodine or of hydriodic acid to the soluble metallic salts.

Iodine often combines in more than one proportion with metals, forming a *protiodide* and a *periodide*.

922. *Action of Iodic Acid.*—The compounds of this acid with the metallic oxides have been but little examined: they are decomposed by heat, sometimes with the evolution of oxygen only; at others, iodine is also given off. Action of Iodic acid.

923. *Action of Hydrogen.*—Hydrogen forms permanent compounds with two of the metals only, namely, arsenic and tellurium. It appears to combine with each in two proportions, forming two solid compounds, the *hydrurets* or *hydrogurets* of arsenic and tellurium; and two gaseous compounds, *arsenuretted* and *telluretted* hydrogen. At high temperatures it dissolves potassium, forming *potassiuretted hydrogen gas*. Action of hydrogen.

There are many of the metallic oxides, and a few of the chlorides, which are decomposed by hydrogen: the oxides are reduced with the formation of water, and the chlorides with the production of muriatic acid.

924. *Action of Water.*—Those metals which are speedily acted upon by common air and oxygen, are also generally susceptible of decomposing water; some of them rapidly, others slowly. There are some metals which are not acted upon by air deprived of moisture, nor by water deprived of air; but moist air, or water containing air, effect their oxidizement: this appears to be the case with iron.* Action of water.

925. The compounds of oxides and water, in which the water exists in a condensed state, are termed *hydrates*, or *hydroxides*, or *hydroxures*. The hydrates of potassa, soda, strontia, and baryta, retain the water which constitutes them such at the temperature of ignition, and it can only, indeed, be expelled by bodies that have a stronger affinity for the alkali or earth. The hydrates of the remaining earths are decomposed by the heat of ignition. Hydrated oxides.

The hydrated oxides of the common metals are obtained by adding a solution of pure potassa, soda, or ammonia to the solution of the oxide in sulphuric, muriatic, or nitric acid. The precipitate washed repeatedly with water, is to be collected on a filter; and if dried, the heat employed must be as gentle as possible; for a slight elevation of temperature is sufficient to expel the whole water and to leave only an oxide.

The hydrated oxides are, for the most part, much more soluble in acids than the oxides. H. 1. 497.

926. *Action of Nitric Acid.*—As the greater number of metals are capable of decomposing nitric acid, and of resolving it into some of the other nitric compounds, nitric acid is a very Action of nitric acid.

* Dr Marshall Hall, *Quart. Jour.* vii. 55.

generally acting solvent of these bodies (509). It dissolves all the metallic oxides and produces a numerous class of *nitrates*, which if prepared with heat and with excess of acid, generally contain the metal at its maximum of oxidizement. The nitrates are all decomposed by a red heat; they give off oxygen, either separate, or combined, and the metallic oxide remains. They are also decomposed when heated with sulphur, phosphorus, or charcoal; and sulphurous, phosphoric, and carbonic acids are formed; the phosphoric, being a fixed acid, remains united to the metallic oxide; while the sulphurous and carbonic acids are usually expelled. The nitrates are decomposed by sulphuric acid, nitric acid is evolved, and *sulphates* are formed.

Proportion
of oxygen in
neutral ni-
trates.

927. In the neutral nitrates the proportion of oxygen in the acid is to that in the base as 5 to 1. Thus in the nitrate of potassa 48 parts of potassa, containing 8 of oxygen, are combined with 54 of nitric acid, containing 40 of oxygen; and in the pernitrate of copper, 80 parts of peroxide of copper containing 16 of oxygen, are combined with 108 of nitric acid, containing 84 of oxygen.

Action of am-
monia.

928. *Action of Ammonia*.—At high temperatures some of the metals are capable of decomposing ammonia. Liquid ammonia dissolves several of the metallic oxides, and with some of them forms crystallizable compounds.

The *ammoniurets* are decomposed by a strong heat; the oxygen of the oxide uniting with the hydrogen of the alkali, and the nitrogen of the latter being set free. In some cases this decomposition is attended with loud explosion.

Action of sul-
phur.

929. *Action of Sulphur*.—Sulphur has a strong tendency to unite with metals. The metallic *sulphurets* are in some cases formed by heating the metal with sulphur; in others, by decomposing the sulphates; and in others, by the action of sulphuretted hydrogen. The sulphurets are in general brittle; some have a metallic lustre; others are without lustre. Some are soluble, others insoluble in water. When the same metal forms two sulphurets, the sulphur in those containing the largest proportion is an exact simple multiple of the sulphur in those containing the smallest proportion. When the metallic sulphurets are heated, some undergo no change, as those of sodium and potassium; others sublime unaltered, as sulphuret of mercury; others lose a portion of their sulphur, and if air be admitted, sulphurous acid escapes and the metal passes into the state of oxide, as sulphuret of lead; others again are entirely decomposed, the metal being completely reduced; this happens on heating sulphuret of platinum or of gold. It is doubtful whether any definite compounds of sulphur with the metallic oxides exist.

Hyposul-
phites.

930. *Hyposulphurous acid* combines with the metallic oxides and produces a class of salts termed *hyposulphites*. Several of these have been examined by Mr Herschel.* In some of their characters they resemble the sulphites: they are easily soluble;

* *Edinburgh Philosophical Journal*, i.

of a bitter or sweet taste; and decomposed by a heat below redness, and by almost all other acids. Their solutions readily dissolve chloride of silver.

931. *Sulphurous acid* combines with many of the metallic oxides, producing *sulphites*; in some instances oxygen is transferred from the oxide to the acid, and sulphates result. Sulphites.

The *sulphites* are soluble in water, and have a sulphurous taste and smell. Exposed to moist air, they absorb oxygen, and pass into the state of sulphates. They are decomposed by sulphuric acid, which expels sulphurous acid, and the salts are converted into sulphates. When perfectly pure they are not affected by solution of baryta.

932. *Sulphuric acid*, in its concentrated state, is acted upon by a few of the metals only; when diluted, some of them are oxidized at the expense of the water, hydrogen is evolved, and the metallic oxide combines with the acid, producing a *sulphate*. Sulphates.
In these cases the hydrogen evolved is the indicator of the quantity of oxygen transferred to the metal; every volume of hydrogen is the equivalent of half a volume of oxygen, and accordingly the production of 100 cubic inches of hydrogen, indicates the transfer of 50 of oxygen, or by weight of about 17 grains. As different metals unite to different weights of oxygen, they will obviously evolve different quantities of hydrogen. Thus, if one metal, to become soluble in sulphuric acid, require to be united with 15, and another with 30 per cent. of oxygen, the latter will evolve twice the volume of hydrogen, compared with the former.

As the evolution of hydrogen, during the solution of a metal in dilute sulphuric acid, is referable to its oxidizement, no hydrogen will be evolved by the action of the acid upon an oxide, but it will be merely dissolved.

The sulphates are an important class of salts. The greater number of them are soluble in water, and the solutions are rendered turbid by solutions of baryta. They are all decomposed at a red heat by charcoal, and most of them are thus converted into sulphurets; carbonic acid, and carbonic oxide, being at the same time evolved.

In the neutral sulphates the proportion of oxygen in the acid is to that in the base as 3 to 1. Thus sulphate of soda is composed of 32 soda containing 8 of oxygen, combined with 40 of sulphuric acid containing 24 of oxygen.

933. *Action of Sulphuretted Hydrogen*.—Sulphuretted hydrogen enters into combination with a few of the metals, with mercury and silver for example, but it unites in general more readily and permanently with their oxides, and forms *hydro-sulphuretted oxides*. Many of these compounds are insoluble, and may be formed by adding a solution of sulphuretted hydrogen, or of hydrosulphuret of ammonia, to solutions of the respective metallic salts. Sometimes, however, a decomposition is effected in these cases, both of the sulphuretted hydrogen and Sulphuretted hydrogen.

of the oxide, and a metallic sulphuret is formed, the hydrogen combining with the oxygen of the oxide to form water, and the sulphur uniting to the metal. In a few cases the metallic oxide is reduced.—For the effect of sulphuretted hydrogen and of hydrosulphuret of ammonia upon solutions of several of the metals, as far as colour of the precipitate is concerned, see *Appendix*.

Action of
phosphorus.

934. *Action of Phosphorus*.—Phosphorus combines with the greater number of the metals, forming a series of *metallic phosphurets*. There are two methods of forming them; either by heating a mixture of phosphorus and the metal, or projecting phosphorus upon the metal previously heated to redness; or by heating a mixture of the metal or its oxide, with phosphoric acid and charcoal. These phosphurets have a metallic lustre; if they contain a difficultly fusible metal they are more fusible than the metal they contain; if an easily fusible metal, less so. They are mostly crystallizable, and totally or partially decomposable at a high temperature.

Phosphates.

935. The *metallic phosphates* may be formed either by dissolving the oxides in phosphoric acid, or by adding a solution of phosphoric acid, or of an alkaline phosphate, to solutions of those metals which form insoluble or difficultly soluble phosphates. The greater number of the phosphates are decomposed by ignition with charcoal; and those containing volatile oxides are volatilized at high temperatures.

In the neutral phosphates the quantity of oxygen in the acid is to that in the base as 2 to 1. Thus phosphate of soda consists of 32 soda containing 8 oxygen, and 28 phosphoric acid containing 16 of oxygen.

Exp.

936. When phosphorus is introduced into the solutions of those metals which have but a feeble attraction for oxygen, it reduces them to the metallic state. Thus gold, silver, and platinum are thrown down by immersing a stick of phosphorus into their respective solutions.

Action of
carbon.

937. *Action of Carbon*.—Carbon unites to very few of the metals, and of the metallic carburets, one only is of importance, namely, carburet of iron, or *steel*.

Carbonates.

938. *Carbonic acid* unites with the greater number of the metallic oxides and forms *Carbonates*, of which the distinctive characters have already been noticed; many of them are of difficult solubility, and may be formed by adding an alkaline carbonate to the metallic solution. Of the carbonates some are entirely, and others only partially decomposed at a red heat. Carbonate of magnesia, for instance, loses the whole of its carbonic acid at a red heat; carbonate of potassa retains it; and bi-carbonate of potassa loses one-half and passes into the state of carbonate.

Action of me-
tals upon each
other.

939. *Action of Metals upon each other*.—The metals may for the most part be combined with each other, forming a very important class of compounds, the *metallic alloys*.

In the new nomenclature, the word ALLOY is retained as a general term for all combinations of metals with each other; and the specific name is derived from that of the metal, which prevails in the compound. Thus in the *alloy of gold with silver*, the gold is to be understood as being in greatest proportion; in the *alloy of silver with gold*, the silver is the principal ingredient.

940. The compounds of mercury with other metals, at a very early period of chemistry, were called AMALGAMS, and as the name does not lead to any erroneous notions, it may still be retained to denote this sort of alloy. H. Alloys.

941. Various processes are adopted in the formation of alloys depending upon the nature of the metals. Many are prepared by simply fusing the two metals in a covered crucible; but if there be a considerable difference in the specific gravity of the metals, the heavier will often subside, and the lower part of the bar or ingot, will differ in composition from the upper; this may be prevented by agitating the alloy till it solidifies. Mr Hatchett found that when an alloy of gold and copper was cast into bars, the moulds being placed perpendicularly, the upper part of the bar contained more copper than the lower.* Process for forming alloys.

When one of the metals is very volatile, it should generally be added to the other after its fusion; and if both metals be volatile, they may be sometimes united by distilling them together.

It has been a question whether alloys are to be considered as compounds, or as mere mixtures. Mr Dalton† considers alloys to be chemical compounds, one striking instance of which is in the alloy of tin and copper called *speculum metal*; the smallest deviations from the true proportions will spoil the alloy as a reflector. In some cases the metals are found to unite in definite proportions only; and it is probable that all the alloys contain a definite compound of the two metals.

942. The principal characters of the alloys are the following:

i. We observe a change in the ductility, malleability, hardness, and colour. Malleability and ductility, are usually impaired, and often in a remarkable degree: thus gold and lead, and gold and tin, form a brittle alloy. The alloy of copper and gold is harder than either of its component parts; and a minute quantity of arsenic added to copper, renders it white. Characters of alloys.

ii. The specific gravity of an alloy is rarely the mean of its component parts; in some cases an increase, in others a diminution of density having taken place,

iii. The fusibility of an alloy is generally greater than that of its components. Thus platinum, which is infusible in our common furnaces, forms, when combined with arsenic, a very fusible alloy; and an alloy of certain proportions of lead, tin, and Fusibility greater than that of their components;

* Phil. Trans. 1803.

† New System of Chem. Philos. part 1st, vol. 2d, as noticed in Edin. Jour. No. xvi.

bismuth is fusible at 212° , a temperature several degrees below the melting point of its most fusible constituent.

More oxidizable.

iv. Alloys are generally more oxidizable than their constituents taken singly; a property which is, perhaps, partly referable to the formation of an electrical combination. Where an alloy consists of two metals, the one easily and the other difficultly oxidizable, it may be decomposed by exposing it to the action of heat and air, the former metal being converted into an oxide; its last portions, however, are often not easily separated, being protected by combination with the least oxidable metal. An alloy of three parts of lead and one of tin is infinitely more oxidizable than either of its components, and easily burns at a dull red heat.

Action of acids on alloys.

v. The action of acids on alloys may generally be anticipated by a knowledge of their effects upon the constituent metals; but if a soluble metal be alloyed with an insoluble one, the former is often protected by the latter from the action of an acid. Thus, silver alloyed with a large quantity of gold, resists the action of nitric acid in consequence of the insolubility of the latter metal in that acid; and, in order to render it soluble, it is requisite that the silver should be made to form about a fourth part of the alloy, in which case the nitric acid extracts it, and leaves the gold in an insoluble film or powder.*

943. Various classifications of the metals have been adopted by chemical authors; some dependent upon their physical, others upon their chemical properties. The former can scarcely be considered as adapted to chemical inquiry, and the latter involve numerous difficulties in consequence of the gradual transition of metals of one class into those of another. We may consider the metals in the order in which they are set down in the following Table, and which is nearly that of their respective attractions for oxygen.

Metals in the order of their attractions for oxygen.

| | |
|-------------|---------------|
| 1 Potassium | 19 Uranium |
| 2 Sodium | 20 Titanium |
| 3 Lithium | 21 Cerium |
| 4 Calcium | 22 Tellurium |
| 5 Barium | |
| 6 Strontium | 23 Arsenic |
| | 24 Molybdenum |
| 7 Magnesium | 25 Chromium |
| 8 Aluminium | 26 Tungsten |
| 9 Manganese | 27 Columbium |
| 10 Iron | |
| 11 Zinc | 28 Nickel |
| 12 Tin | 29 Mercury |
| 13 Cadmium | 30 Osmium |
| | 31 Iridium |
| 14 Copper | 32 Rhodium |
| 15 Lead | 33 Palladium |
| 16 Antimony | 34 Silver |
| 17 Bismuth | 35 Gold |
| 18 Cobalt | 36 Platinum |

* This constitutes the process of *Quartation*.

SECTION II. *Potassium.*

1944. This metal was discovered in 1807 by Sir H. Davy.*
 He obtained it by submitting caustic potassa, or potash, to the action of Voltaic electricity: the metal was slowly evolved at the negative pole.

Discovery.

945. To this discovery and others of a similar kind Sir H. Davy was led by a train of inductive reasoning, which is not surpassed by any investigation in the history of the physical sciences. From the facts which had become known respecting the powers of electrical decomposition, it appeared to be a natural inference, that the same powers applied in a state of the highest intensity, might disunite the elements of some bodies, which had resisted all other instruments of analysis. If potassa, for example were an oxide, composed of oxygen united to an inflammable base, it seemed probable that when subjected to the action of opposite electricities, the oxygen would be attracted by the positive wire and repelled by the negative. At the same time, the reverse process might be expected to take place with respect to the combustible base, the appearance of which might be looked for at the negative pole.

Its existence
how inferred.

946. In his first experiments, suggested by these views, Sir H. Davy failed to effect the decomposition of potassa, owing to his employing the alkali in a state of aqueous solution, and to the consequent expenditure of the electrical energy in the mere decomposition of water. In his next trials, the alkali was liquefied by heat in a platinum dish, the outer surface of which, immediately under the alkali, was connected with the zinc or positive end of a battery consisting of 100 pairs of plates, each six inches square. In this state the potassa was touched with a platinum wire proceeding from the copper or negative end of the battery; when instantly a most intense light was exhibited at the negative wire, and a column of flame arose from the point of contact, evidently owing to the developement of combustible matter. The results of the experiments could not, however, be collected, but were consumed immediately on being formed.

Davy's experiments.

947. The chief difficulty in subjecting potassa to electrical action is, that, in a perfectly dry state, it is a complete non-conductor of electricity. When rendered, however, in the least degree moist by breathing on it, it readily undergoes fusion and decomposition, by the application of strong electrical powers. For this purpose, a piece of potassa, weighing from 60 to 70 grains, may be placed on a small insulated plate of platinum, and may be connected, in the way already described, with the opposite end of a powerful electrical battery, containing not less than 100 pairs of six inch plates. On establishing the connexion, the potassa will fuse at both places, where it is in contact with the platinum. A violent effervescence will be seen at

Method of obtaining potassium by electricity.

* *Philos. Trans.* 1808.

the upper surface, arising, as Sir H. Davy has ascertained, from the escape of oxygen gas. At the lower or negative surface, no gas will be liberated; but small bubbles will appear, having a high metallic lustre, and being precisely similar in visible characters to quicksilver. Some of these globules burn with an explosion and bright flame; while others are merely tarnished, and are protected from farther change by a white film, which forms on their surface.

Produced in
vacuo.

This production of metallic globules is entirely independent of the action of the atmosphere; for Sir H. Davy finds, that they may be produced *in vacuo*.

How pre-
served.

948. To preserve this new substance, it is necessary to immerse it immediately in pure naphtha, a fluid which will be described in a subsequent part of the work. If exposed to the atmosphere, it is rapidly converted back again into the state of pure potassa. To prevent its oxidation still more effectually, Mr Pepys has proposed to produce it under naphtha; and has contrived an ingenious apparatus for this purpose, which is described in the 31st volume of the *Philosophical Magazine*, page 241.

949. Nothing can be more satisfactory than the evidence furnished by these experiments, of the nature of one of the fixed alkalis. By the powerful agency of opposite electricities, it is resolved into oxygen and a peculiar base. This base like other combustible bodies, is repelled by positively electrified surfaces, and attracted by negative ones; and hence its own natural state of electricity must necessarily be positive. Again, by uniting with oxygen, it is once more changed into alkali, either slowly at ordinary temperatures; or with heat and light, at high temperatures. We have the evidence, therefore, both of analysis and synthesis, that potassa is a compound of oxygen with a peculiar inflammable basis.

Reasons for
considering
it a metal.

950. In assigning to this newly discovered substance a fit place among the objects of chemistry, Sir H. Davy was induced to class it among the metals, because it agrees with them in opacity, lustre, malleability, conducting powers as to heat and electricity, and in its qualities of chemical combination. The only property which can be urged against this arrangement, is its extreme levity, which even exceeds that of water. But when we compare the differences which exist among the metals themselves, this will scarcely be considered as a valid objection. Tellurium, for example, which no chemist hesitates to consider as a metal, is only about six times heavier than the base of potassa, while it is four times lighter than platinum; thus forming a sort of link between the old metals and the bases of the alkalis.

951. In giving names, therefore, to the alkaline bases, Sir H. Davy has adopted that termination, which, by common consent, has been applied to other newly discovered metals, and which, though originally Latin is now naturalized in our language.

The base of potassa he has called POTASSIUM, and the base of soda, SODIUM; and these names have met with universal acceptance among chemical philosophers.

952. *Process for preparing Potassium.*—It is not, however, by electrical means only that the decomposition of potassa has been accomplished. Soon after Sir H. Davy's discoveries were known at Paris, Messrs Gay-Lussac, and Thenard* succeeded in their attempts to decompose both the fixed alkalies, without the aid of a Voltaic apparatus, merely by the intervention of chemical affinities. Their process, though it affords the alkaline bases of less purity, yields them in much larger quantity, than the electrical analysis, viz. to the amount of nearly 400 grains by one operation. It consists in bringing the alkalies into contact with intensely heated iron, which, at this temperature, attracts oxygen more strongly than the alkaline base retains it.

Other processes for obtaining potassium.

The apparatus used for obtaining potassium, has a general resemblance to that which is employed for decomposing water by means of iron. It consists of a gun-barrel curved as in fig. 120, which is copied from Thenard's *Trailé de Chimie*. At one end the barrel is drawn out to rather a smaller diameter; and, before being used, it is to be covered between *b* and *f*, with a lute of infusible clay,—(the lute may consist of five parts sand and one potters' clay)—which should be suffered to dry thoroughly. Into the barrel between *f* and *b*, clean iron turnings are to be introduced, and between *a* and *b* pieces of solid hydrate of potassa. A tube of safety is to be luted to the end *a*, and is to be immersed in mercury in the glass vessel *m*. To the smaller end of the barrel, a short piece of copper tube, *g*, is accurately ground, and to this last a small copper receiver, *h*, destined to collect the potassium, is fitted by grinding. To the other end of *h*, a tube of safety, *i*, is to be luted, and made to dip into mercury contained in the vessel *l*, but to a less depth than the safety tube *m*.

Apparatus for obtaining potassium.

Pl. vii.

A strong heat, is now to be raised in the furnace, and, while this is doing, the part of the barrel containing the potassa, as well as the end *f*, and the attached copper tube and receiver, should be kept cool by wet cloths. If gas now issues abundantly through the safety tube *i*, the junctures may be concluded to be tight. When the barrel has become white hot, the potassa may be melted by burning charcoal contained in a moveable cage *k*. It will then flow upon the intensely ignited iron turnings, and a large quantity of hydrogen gas, holding some potassium in solution, will issue through the safety tube, *i*. The cage may now be removed for a short time; and, when the production of gas slackens, it may be restored to its place. These operations may be repeated alternately till no more gas is evolved; after which the heat in the furnace should be made as intense as possible, in order to drive off some of the potassium which strongly adheres to the iron turnings. If the escape of the gas through *i*, should at any time cease during the operation, and take place through *m*, this will probably be owing to a lodgment of potassium at the end *f*, of the barrel, from which it may be melted into the copper receiver, by holding a little red-hot charcoal under the part where it has condensed.

At the close of the operation, as soon as the vessels *g* and *h* are sufficiently cool, they are to be removed, then filled with naphtha, emptied again, and quickly stopped with corks. As a portion of potassium generally remains in the portion *f*, the barrel should also be plugged by an iron stopper provided for the purpose. When sufficiently cold it may be removed from the furnace, and a little naphtha passed through it. The potassium must be detached in as large pieces as possible from the barrel, and from the copper receiver, and be kept under rectified naphtha in a well-stopped phial.

953. When the iron turnings are very clean, the potassa very dry and pure, and the whole apparatus free from foreign matters,

* *Annales de Chimie*, lxx. 325; or *Memoirs d'Arcueil*, ii. 299.

the metal produced differs very little from that obtained by a Voltaic battery. Its lustre, ductility, and malleability are similar. Its point of fusion and specific gravity, however, are a little higher; for it requires nearly 130° Fahr. to render it perfectly fluid, and is to water as 796 to 1000 at 60° Fahrenheit. This Sir H. Davy ascribes to contamination with a minute proportion of iron. The affinities, indeed, by which the decomposition is produced, he supposes to be those of iron for oxygen, of iron for potassium, and of potassium for hydrogen.*

Mr Bruner's
process.

954. The great difficulty in this process consists in protecting the gun-barrel from the effects of the violent heat which is necessary to decompose the alkali. To guard it from injury, a hollow cylinder, made of Stourbridge clay, has been found to answer much better than lute.† The success of the operation is, however, more effectually secured by an improvement of M. Brunner, which enables us to perform it at a lower temperature.‡ The retort employed by him is a spheroidal iron bottle, about half an inch in thickness, and capable of holding about a pint of water, into the shorter end of which a gun-barrel bent into this form (P) is screwed. When the retort is charged and luted, it is placed in a furnace; so that the longer leg of the bent gun-barrel may pass out at the bottom or in front, in a direction nearly perpendicular, the bent part itself remaining in the furnace, and being wound round with iron wire to protect it from the fire. The receiver is a cylindrical copper vessel with an opening at the top to admit the end of the gun-barrel, and a tube passing from the side to convey away the gas produced in the operation. It is placed, when in use, in water or in ice. The decomposition of the potassa, M. Brunner finds is greatly facilitated by employing charcoal along with the iron. Into the retort, after being cleaned, dried, and heated, four ounces of fused caustic potassa were introduced, in small portions alternately with six ounces of iron turnings broken in a mortar and mixed with one ounce of pulverized charcoal. The whole was stirred together, and covered with two ounces of iron turnings; and the retort being luted and the barrel adapted, the fire was lighted and gradually raised. In half an hour, the green vapours of potassium appeared in a

Mr Tennant's
apparatus.

* Mr Tennant's apparatus by which we can obtain potassium with the heat of a common forge, fig. 121, consists of a gun barrel *a*, eighteen inches long, closed at one end, and whose thickest part is widened by means of a hammer; it is coated externally with a lute similar to that mentioned in the preceding apparatus; the mixture of potassa and cuttings of iron proper to furnish the potassium is introduced, and the tube is fixed with a certain inclination in a reverberatory furnace or forge *f*; in the upper part of the barrel is inserted a narrower tube *t*, seven or eight inches long, having a small hole at its lower end, in which the vaporized potassium ought to pass: this tube should not be entirely inserted in the former; about an inch should extend beyond it, in order to remove it with more ease; at its upper end an empty tube *v*, is fixed and closed with a cork, through which passes a bent glass tube *r*, in which a little mercury is put. The part of the tube *c*, *d*, which is out of the furnace, should be kept in wet linen or brown paper, to facilitate the condensation of the metal. Things being so disposed, a strong heat is applied about an hour, and the potassium is obtained in the tube *t*.

† *Ann. of Phil. N. S.* vi. 233.

‡ *Quart. Jour.* xv. 279.

glass tube, which had been attached to the end of the barrel for the purpose of watching the process. The receiver containing naphtha was now applied, so that the end of the barrel dipped into the fluid. An immense production of gas took place which frequently took fire spontaneously and burned with a violet flame and white fumes. In twenty-five minutes from the application of the receiver, the gas diminished in quantity, and soon entirely ceased coming over. The receiver was then separated, and found to contain 150 grains of potassium. Eight ounces of fused subcarbonate of potassa, six ounces of iron filings, and two ounces of charcoal, similarly treated, gave 140 grains of potassium. Crude tartar (impure bi-tartrate of potassa) was found also to yield potassium in the proportion of 150 grains from 12 ounces of tartar. The substitution of the two last mentioned salts makes the process much more economical; and the employment of charcoal renders so much lower a heat necessary than for the common method, that the same apparatus served for as many as thirty operations. In potassium, however, which had thus been obtained from the subcarbonate, Berzelius found some admixture of charcoal.*† H. 1. 521.

955. Potassium is a white metal of great lustre. It exists in small globules, which possess the opacity, and general appearance of mercury; so that when a globule of mercury is placed near one of potassium the eye can discover no difference between them. It instantly tarnishes by exposure to air. It is ductile, and of the consistency of soft wax. Properties.

Its specific gravity is 0,865. At 150° it enters into perfect fusion; and at a bright red heat rises in vapour. At 32° it is a hard and brittle solid. If heated in air it burns with a brilliant white flame. It is an excellent conductor of electricity and of heat.

956. *Potassium and Oxygen.*—When potassium is thrown into water, or upon a piece of ice, it instantly takes fire; hydrogen gas is evolved, and *oxide of potassium, or potassa*, is found dissolved in the water.—The quantity of hydrogen evolved in this experiment becomes the indicator of the proportion of oxygen which has been transferred to the metal; 100 parts of potassium are thus found to absorb 20 of oxygen; and if this be considered a protoxide, then $20 : 100 :: 8 : 40$.—so that 40 will be the number representing potassium, and 40 P. + 8 O. = 48 will represent dry oxide of potassium. (B)—When water is made to act on the base of potassa, atmospheric air being excluded, there is much heat and noise, but no luminous appearance, and the gas evolved is pure hydrogen. Each grain of potassium, by acting on water, detaches about 1,06 cubic inches of hydrogen gas. H. Combination with oxygen.
Exp.

* *Ann. de Chim. &c.* xxvii. 340.

† M. Van Mons has applied the residue obtained by decomposing nitre by heat to the preparation of potassium. See *Quart. Jour.* 44, 405.

Exp.

957. The production of alkali, by the action of water on potassium, is most satisfactorily shown, by dropping a globule of the metal upon moistened paper, which has been tinged with turmeric. At the moment when the globule comes into contact with the paper, it burns, and moves rapidly, as if in search of moisture, leaving behind it a deep reddish-brown trace, and acting upon the paper exactly like dry caustic potassa. So strong, indeed, is the affinity of potassium for oxygen, that it discovers and decomposes the small quantities of water contained in alcohol and ether, even when carefully purified, and disengages from both these fluids, hydrogen gas. H. 1. 524.

Potassa.

958. Potassa, in the state it is usually met with in laboratories, contains a considerable portion of water, from which it may be freed by the action of iron at high temperatures, and there always remains in the barrel, after the above experiment, a large portion of *dry potassa*. It is a hard grey substance, which, by water, is slowly converted into the *hydrated oxide*, or caustic potash, which may be obtained by evaporation. This substance, after exposure to a red heat, is white and very soluble in water; it may be considered as a compound of 1 proportional of protoxide of potassium = $48 + 1$ proportional of water 9, and its number = 57.

Peroxide.

959. *Peroxide of Potassium*.—If the metal be heated in considerable excess of oxygen, it burns with intense heat and light, and an orange-coloured substance is obtained, which consists of 40 potassium + 24 oxygen = 64. This peroxide of potassium, when put into water, effervesces, oxygen is given off and a solution of the hydrated protoxide is obtained. Peroxide of potassium is also formed by passing oxygen over potassa heated to redness.

Mode of procuring caustic potassa.

960. The *hydrated protoxide* or *caustic potash*, is procured in our laboratories by decomposing its carbonate by lime. The best process consists in boiling in a clean iron vessel, carbonate of potassa, (obtained by calcining tartar) with half its weight of pure quick-lime, in water. The ley is strained through clean linen, concentrated by evaporation, again strained, and set by in a well-stopped bottle till it admits of being decanted clear from the sediment. The clear solution is to be evaporated to dryness. It is often cast into sticks for the use of surgeons, who employ it as a caustic, and in this state it generally contains some peroxide, and therefore evolves oxygen when dissolved in water. It is the *potassa fusa* of the *London Pharmacopœia*. It may be further purified by the action of alcohol, which dissolves the pure hydrate and leaves earthy and other impurities; the alcohol is then driven off by heat. In this case the alcohol is always in some measure acted upon by the potassa, and a portion of carbonaceous matter deposited, so that it should be allowed to remain as short a time as possible combined with the alkali. Having obtained the dry caustic alkali by lime, it

may be boiled in a silver basin with highly rectified alcohol for a few minutes, and then set by in a stopped phial; when the impurities are deposited, the alcoholic solution may be poured off and rapidly evaporated to dryness in a silver basin as before: the heat may then be raised so as to fuse the potassa, which, on cooling, should be broken up and preserved in well-closed phials.*

Hydrate of Potassa thus purified is white, very acrid and corrosive, and at a bright red heat evaporates in the form of white acrid smoke. It quickly absorbs moisture and carbonic acid from the air, and at 60° one part of water dissolves two.† It may be crystallized in octoëdrons. It is highly alkaline, and being exclusively procured from vegetables was formerly called *vegetable alkali*. When touched with moist fingers it has a soapy feel, in consequence of its action upon the cuticle. In the fused state it produces heat when dissolved in water; but in its crystallized state it excites considerable cold, especially when mixed with snow. At a natural temperature of 30° , M. Lowitz found that equal weights of crystallized potassa and snow depressed the thermometer 45° .‡

Characters.

961. Potassa may be distinguished from all other substances by the following characters. 1. If tartaric acid be added in excess to a salt of potassa dissolved in water, and the solution be stirred with a glass rod, a white precipitate, the bitartrate of potassa, soon appears, which forms peculiar white streaks upon the glass by the pressure of the rod in stirring. 2. A solution of the muriate of platinum causes a yellow precipitate, the muriate of platinum and potassa. This is the most delicate test, provided the mixture be gently evaporated to dryness, and a little cold water be afterwards added. The muriate of platinum and potassa then remains in the form of small shining yellow crystals. 3. By being precipitated by no other substance.§

Potassa, how distinguished.

962. *Chlorine and Potassium* act very energetically upon each other, and produce the white compound which has been called *muriate of potash*, but which is a true *chloride of potassium*. According to Sir H. Davy it is constituted of 75 potas-

Chloride.

* Mr Donovan has proposed the following as a more easy method of obtaining pure potassa. The crystallized bi-carbonate of potassa of the shops is to be purified by dissolving it in water at the temperature of 130° . The saturated solution must be filtered and poured into a flat dish, and placed before the fire; in a few hours a crop of crystals of the pure bi-carbonate will be obtained. They may then be rinsed with a very small quantity of water, and dried on blotting paper. The crystals are now to be dissolved in water, and boiled with their own weight of hydrate of lime for 15 minutes; the liquid is then to be filtered and we have at once a solution of pure potassa which may be evaporated as above. See *Boston Jour. of Philos.* iii. 96.

† For a table of the quantity of real potassa contained in solutions of different specific gravities, see *Appendix*.

‡ *Annales de Chimie*, xxii.

§ *Turner*.

Mix five grains of the salt with half the quantity of powdered charcoal in a similar manner. On triturating the mixture strongly, it will inflame, especially with the addition of a grain or two of sulphur, but not with much noise. Exp.

967. When sulphuric acid is poured upon mixtures of this salt and combustibles, instant ignition ensues in consequence of the evolution of oxide of chlorine; and when sulphuric or nitric acids are poured upon similar mixtures under water by means of a long funnel, inflammation also ensues. Action of sulphuric acid.

Mix a small quantity of sugar with half its weight of the salt, and on the mixture pour a little sulphuric acid.* A sudden and vehement inflammation will be produced. This experiment, as well as the following, requires caution. Exp.

To one grain of the powdered salt, add about half a grain of phosphorus, wrap them in tin foil, and place upon an anvil, on striking the mixture with a hammer the phosphorus will detonate, with a very loud report. The hand should be covered with a glove in making this experiment, and care should be taken that the phosphorus, in an inflamed state, does not fly into the eyes. Exp.

Phosphorus may also be inflamed under the surface of water, by means of this salt. Put into a wine glass, one part of phosphorus with two of the salt; fill it nearly with water, and pour in, by means of a glass tube, reaching to the bottom, three or four parts of sulphuric acid. The phosphorus takes fire, and burns vividly under the water. This experiment too requires caution lest the inflamed phosphorus should be thrown into the eyes.† Oil may also be thus inflamed on the surface of water, the experiment being made with the omission of the phosphorus, and the substitution of a little olive or linseed oil. Exp.

968. Chlorate of potassa should not be kept mixed with sulphur in considerable quantity, as the mixture may explode spontaneously.

969. It was proposed by Berthollet to substitute this salt for nitre, in the preparation of gunpowder and the attempt was made at Essone in 1788; but, as might have been expected, no sooner was the mixture of the chlorate with the sulphur and charcoal submitted to trituration than it exploded with violence, and proved fatal to several people. With phosphorus the detonation is dangerously violent. These phenomena depend upon the decomposition of the chloric acid and the evolution of peroxide of chlorine (323). Substituted for nitre in gunpowder.

970. A few grains of chlorate of potassa put into a tea-spoonful of muriatic acid, and then diluted with water, form an extemporaneous bleaching liquor.

971. By Gay-Lussac, the chlorates are considered as compounds of chloric acid with alkaline and earthy bases; by Sir H. Davy, they are regarded as triple compounds of 1 atom of chlorine, 1 atom of metallic base, and 6 atoms of oxygen. But chloric acid being, as is deducible from the experiments of Gay-Lussac, compounded of five atoms of oxygen with 1 of chlorine; there is no difference as to the facts, whatever there may be as to their explanation. This will appear from the following comparative statement.

* A mixture of this kind is the basis of the matches, now generally used for the purpose of procuring instantaneous light. The bottle into which they are dipped, contains concentrated sulphuric acid which is prevented from escaping by a quantity of finely spun glass or the fibres of amianthus:

† Davy.

According to Davy,

Chlorates consist of $\left\{ \begin{array}{l} 1 \text{ atom of metallic base} \\ 1 \text{ " " chlorine} \\ 6 \text{ atoms " oxygen.} \end{array} \right.$

According to Gay-Lussac,

Chlorates are $\left\{ \begin{array}{l} 1 \text{ atom of base} \\ \text{consisting of} \\ 1 \text{ atom of chloric} \\ \text{acid} \end{array} \right. \left\{ \begin{array}{l} 1 \text{ atom metal} \\ 1 \text{ " oxygen} \\ 5 \text{ atoms oxygen} \\ 1 \text{ atom chlorine.} \end{array} \right.$

It will be perceived on examining these statements, that the same proportions of elements are assigned by both philosophers to the chlorates, and that the only difference is as to the manner in which those elements are arranged. H. 1. 534.

972. When chlorate of potassa is distilled in a coated glass retort, it first fuses, and on a farther increase of temperature, yields oxygen gas of great purity. A hundred grains afford 75 cubic inches of gas (= about $25\frac{1}{2}$ grains) containing not more than 3 per cent. of nitrogen gas.

Perchlorate. 973. *Perchlorate of Potassa* may be formed by moistening one part of chlorate of potassa with three of sulphuric acid, and carefully heating the mass till it becomes white: in this state it consists of bisulphate and oxychlorate of potassa, which may be separated by solution and crystallization, the former being much more soluble in cold water than the latter salt.

Oxychlorate of potassa does not change vegetable colours. It requires more than 50 parts of water at 60° for its solution. It is insoluble in alcohol. It crystallizes in elongated octoëdrons. When mixed with its own weight of sulphuric acid, and distilled at 280° , solution of perchloric acid passes over. It may be decomposed by exposure to a temperature of 412° , oxygen is given off, and chloride of potassium remains. It consists of one proportional of perchloric acid and one proportional potassa.*

Iodate. 974. *Iodate, and Hydriodate of Potassa*.—Both these salts are formed by agitating iodine with a solution of potassa; water is decomposed, and gives origin to a very soluble hydriodate and a difficultly soluble iodate. The latter may be purified by being washed first with a little water, and afterwards with alcohol sp. gr. .820, which removes the hydriodate. The iodate remains in small white and granular crystals.

When projected on red-hot coals, iodate of potassa burns like saltpetre; 100 parts heated in a retort give 22,59 oxygen gas, and 77,41 iodide of potassium. It requires for solution $13\frac{1}{2}$ parts of water at 60° Fahrenheit. It is constituted of 22,246 potassa and 77,754 iodic acid.

975. The *hydriodate of potassa* is easily made by neutralizing hydriodic acid with pure potassa; but in preparing a considerable quantity of the salt as for medical use, it is desirable to dispense with the preliminary step of making the acid.

* Bromate of Potassa, (340).

With this view the following process has been described by Dr Turner.*

To a hot solution of pure potassa add as much iodine as it is capable of dissolving; a deep brownish-red coloured fluid will be formed, consisting of the iodate and hydriodate of potassa together with a large excess of free iodine. Transmit a current of sulphuretted hydrogen through the solution until the free iodine and iodic acid are converted into hydriodic acid, changes which may be known to be accomplished by the liquid becoming quite limpid and colourless. The solution is then gently heated, to expel any excess of sulphuretted hydrogen, and after being filtered, the pure hydriodic acid is exactly neutralized by pure potassa.

976. Hydriodate of potassa is deliquescent, and consequently very soluble. It is constituted of 100 hydriodic acid + 37,426 potassa. By crystallization, or simple desiccation, it is changed into iodide of potassium, which is easily fused and volatilized without change at a red heat. H. 1. 538. Hydriodate.

977 *Potassium and Hydrogen*.—When potassium is heated in hydrogen, it absorbs a portion of the gas, and produces a grey and highly inflammable *hydruret*. When hydrogen and potassium are passed together through a white hot tube, the gas dissolves the metal, and produces a spontaneously inflammable *potassiuretted hydrogen gas*. Both these compounds are usually formed during the operation for obtaining potassium by the gun-barrel. Hydruret.

978. *Nitrate of Potassa—Nitre—Saltpetre*.—This salt is an abundant natural product, and is principally brought to this country from the East Indies, where it is produced by lixiviation from certain soils. Nitrate.

The rough nitre imported from the East Indies is in broken crystals of a brown colour, and more or less deliquescent: exclusive of other impurities, it often contains a very considerable proportion of common salt, which reacting upon the nitre, induces the production of nitrate of soda and chloride of potassium.

979. In Germany and France it is artificially produced in what are termed nitre-beds. Thenard† has described the French process at length. It consists in lixiviating old plaster rubbish, which when rich in nitre, affords about five per cent. Refuse animal and vegetable matter which has putrefied in contact with calcareous soils produces nitrate of lime, which affords nitre by mixture with subcarbonate of potassa. In the same way it is abundantly produced in some parts of Spain. Exudations containing saltpetre are not uncommon upon new walls, where it appears to arise from the decomposition of animal matter contained in the mortar. It was long ago shown by Glauber, that a vault plastered over with a mixture of lime, wood-ashes, and cows' dung, soon becomes covered with efflorescent nitre, and that after some months, the materials yield, on lixiviation, a considerable proportion of that salt. Artificial production of nitre.

* *Edin. Med. and Surg. Jour.* July, 1825.

† *Traité de Chimie Élémentaire*, Tom. ii. p. 511.

Characters.

Nitre crystallizes in six-sided prisms, usually terminated by dihedral summits; it dissolves in 7 parts of water at 60° and in its own weight at 212° . Its taste is cooling and peculiar. It consists of one proportional of acid = 54 + one proportional of potassa = 48.

Effect of heat.

980. When exposed to a white heat, nitre is decomposed into oxygen, nitrogen, and dry potassa. By distilling it in an earthen retort, or in a gun-barrel, oxygen gas may be obtained in great abundance, one pound of nitre yielding about 12,000 cubic inches of sufficient purity for common experiments, but not for purposes of accuracy. It fuses at a heat below redness, and congeals on cooling into cakes called *sal prunelle*.

If the temperature of nitre be so far increased as to allow a portion of oxygen to escape, the remaining salt, as Scheele first observed, remains neutral, and in this state it has been considered as forming a *nitrite of potassa*.

Decomposed
by charcoal,

981. Nitre is rapidly decomposed by charcoal at a red heat. This may be shown by mixing two parts of powdered nitre with one of powdered charcoal, and setting fire to the mixture in an iron vessel under a chimney.—If excess of charcoal be used, the results are carbonic oxide and acid, nitrogen, and sub-carbonate of potassa, formerly called *nitrum fixum*, and *white flux*.

The old chemists used to perform this detonation in retorts connected with capacious receivers, which were generally blown to pieces; sometimes they succeeded in obtaining a little acidulated water, which they called *clyssus of nitre*, and attributed to it wonderful medical virtues.

and by sulphur.

982. Nitrate of potassa is also decomposed by sulphur, with different results, according to the temperature and proportions employed.

Exp.

Mix powdered nitre and sulphur, and throw the mixture, by a little at a time, into a red-hot crucible. The sulphur will unite with the oxygen of the nitric acid, and form sulphuric acid; which, combining with the potassa, will afford sulphate of potassa. The production of the latter salt will be proved by dissolving the mass remaining in the crucible, and crystallizing, when a salt will be obtained exhibiting the characters of the sulphate.

Exp.

Pl. 2.

Mix a portion of sulphur with one sixth or one eighth its weight of nitrate of potassa; put the mixture into a tin cup; and raise it, by a proper stand, (fig. 36,) a few inches above the surface of water, contained in a flat shallow dish. Set fire to the mixture, and cover it with a bell-shaped receiver. In this case also, sulphuric acid will be formed; but it will not combine, as before, with the alkali of the nitre, which alkali is present in sufficient quantity to absorb only a part of the acid produced. The greater part of the acid will be condensed on the inner surface of the glass bell, and by the water, which will thus become intensely acid. The operation may be repeated three or four times, using the same portion of water. When the water is partly expelled, by evaporation in a glass dish, concentrated sulphuric acid remains. H.

When phosphorus is thrown upon nitre, and inflamed, a vivid combustion ensues, and a phosphate of potassa is formed. Sulphur sprinkled upon hot nitre burns, and produces a mixture of sulphate and sulphite of potassa. This salt used formerly to be employed in medicine, under the name of *Glaser's polychrest*.

salt. Most of the metals, when in filings or powder, detonate and burn when thrown on red-hot nitre; some of the more inflammable metals produce in this way a considerable explosion.

983. A mixture of three parts of nitre, two of dry subcarbonate of potassa, and one of sulphur, forms *fulminating powder*. If a little of this compound be heated upon a metallic plate, it blackens, fuses, and explodes with much violence, in consequence of the rapid action of the sulphur upon the nitre.

984. *Gunpowder* consists of a very intimate mixture of nitre, sulphur, and charcoal. The proportions vary. The following are those usually employed :

| | Common Gunpowder. | Shooting powder. | Shooting powder. | Miners powder. |
|---------------|----------------------|---------------------|---------------------|-------------------|
| Saltpetre . . | 75,0 | 78 | 76 | 65 |
| Charcoal . . | 12,5 | 12 | 15 | 15 |
| Sulphur . . | 12,5 | 10 | 9 | 20 |

The latter contains the smallest quantity of saltpetre, as it requires less *quickness* or *strength*. The ingredients are *perfectly* mixed, moistened, beaten into a cake which is afterwards broken up, granulated, dried, and for the finest powder polished by attrition. The violence of the explosion of gunpowder depends upon the sudden production of gaseous matter, resulting from the action of the combustibles upon the nitre. Carbonic oxide, carbonic acid, nitrogen, and sulphurous acid, are the principal gaseous results; and the solid residue consists of sub-carbonate, sulphate, and sulphuret of potassa, and charcoal.*

Gunpowder may be inflamed by a violent blow; if mixed with powdered glass, or any other harder substance, and struck with a heavy hammer upon an anvil, it almost always explodes.†

985. *Potassium and Sulphur*.‡—When potassium is fused with sulphur, in a vessel filled with the vapour of naphtha, a rapid combination ensues, accompanied with heat and light, and a disengagement of sulphuretted hydrogen. The result is a grey *sulphuret of potassium* not unlike artificial sulphuret of iron. Its formation and properties have been investigated by Vauquelin.§

986. Sulphuret of potassium has, when moistened, a disagreeable smell, and an offensive taste. It is very soluble in water, and the solution blackens the skin, and turns syrup of violets green, like an alkali. All acids, even the weakest, precipitate

* Cruickshanks, *Nicholson's Journal*, iv.

† Iron has been excluded from powder mills as subject to cause sparks by a blow, and brass and copper have been used in its place. It has been found by Col. Aubert that brass on brass can inflame gunpowder, as also iron against iron; iron against brass, iron against marble; lead against lead or against wood when the blow is produced by a leaden ball shot from a fire-arm. The blow of an iron hammer against lead or wood has not as yet inflamed powder—*Bull. Univ.*

‡ *Bromine and Potassium*.—The bromuret of potassium may be obtained in cubic crystals from the hydro-bromate of potassa by evaporation, and was found by M. Balard to consist of

| | | |
|-----------|-----------|-------|
| Bromine | - - - - - | 65,56 |
| Potassium | - - - - - | 34,44 |

§ *Ann. de Chim. et de Phys.* vi. 22.

sulphur from it, and the stronger acids, when previously diluted, occasion a disengagement of sulphuretted hydrogen gas. The solution absorbs oxygen gas and has been employed in eudiometry. According to Vauquelin 100 of potassa unite with 111,5 of sulphur. Berzelius finds that 100 parts of the carbonate absorb 23,9 parts of sulphur.*

Hydro sulphuret.

987. *Hydro-sulphuret of potassa* may be formed by transmitting a current of sulphuretted hydrogen gas through liquid hydrate of potassa, which acquires a yellow colour, and an offensive smell. It forms large transparent crystals, not unlike those of sulphate of soda, but having the shape of four-sided prisms acuminated with four planes, or six-sided prisms acuminated with six planes. It is deliquescent, and runs into a thick syrupy liquor, which gives a green colour to the skin. It dissolves readily in water and alcohol, with a production of cold. On adding any diluted acid, abundance of sulphuretted hydrogen is disengaged, but no sulphur is deposited.

Hydroguretted sulphuret.

988. *Hydroguretted sulphuret of potassa* may be formed by boiling flowers of sulphur in liquid hydrate of potassa, or by digesting sulphur with the liquid hydro-sulphuret. The resulting product may be considered as a compound of bi-sulphuretted hydrogen with potassa, in proportions not yet ascertained. By mere solution in water, the sulphuret of potassa is partly changed into this substance. According to Proust, red oxide of mercury, digested with hydroguretted sulphurets, removes the sulphuretted hydrogen, and what remains is a pure liquid sulphuret. H. 1. 549.

Hypo-sulphite.

989. *Hypo-sulphite of Potassa*.—This salt is best formed by exposing the hydroguretted sulphuret to the atmosphere, till it has lost its colour, after which, on evaporation, it crystallizes in the form of fine needles; or by decomposing hydro-sulphuret, or hydroguretted sulphuret of potassa by sulphurous acid. The salt has a taste, at first, not unlike that of nitre, succeeded by bitterness, and it is deliquescent. When carefully dried, it takes fire on raising the heat, and burns somewhat like tinder, but with a feeble blue flame. It dissolves chloride of silver, even when very dilute, with great readiness.

Sulphite.

990. *Sulphite of Potassa* is formed by passing sulphurous acid into a solution of carbonate of potassa till all effervescence ceases, and evaporating out of the contact of air. Rhomboidal plates are obtained, white, of a sulphurous taste, and very soluble. By exposure to air, they pass into sulphate of potassa.

From Dr Thomson's analysis it is constituted in 100 parts, of 2 water + 54,5 base + 43,5 acid; or 100 of sulphurous acid unite with 150 of potash.

Sulphate.

991. *Sulphate of Potassa* may be formed by saturating carbonate of potassa, with sulphuric acid, and crystallizing the solu-

* Berzelius has described four other compounds which he obtained by igniting carbonate of potassa with different proportions of sulphur. These are composed of 1 atom potassium to 2, 3, 4 and 5 atoms of sulphur.

tion. It is a refuse product also of several chemical operations carried on upon a large scale in the processes of the arts. It is the *sal de duobus* of the old chemists: the *potassæ sulphas* of the *U. S. Pharmacopœia*. Its taste is bitter. It crystallizes in short six-sided prisms, terminated by six-sided pyramids. The body of the prism is often wanting and the triangular-faced dodecaëdron results. This salt dissolves in 16 parts of cold, and 5 of boiling water, and in consequence of its difficult solubility, it is thrown down in a white granular powder when sulphuric acid is added to a moderately strong solution of potassa. Exposed to a red heat it melts, but is not decomposed.

Characters.

992. Sulphate of potassa is decomposed at high temperatures, by charcoal. Mix any quantity of the salt with one fifth of its weight of charcoal finely powdered, and expose the mixture, in a crucible, to a strong heat. The carbon will unite with the oxygen of the sulphuric acid, and escape in the state of carbonic acid gas. What remains is a compound of sulphur and potassium. Sulphate of potassa consist of

Decomposition.

1 proportional of acid = 40
1 ----- potassa = 48
88

993. *Bi-sulphate* or *Supersulphate of Potassa* is formed by adding sulphuric acid to a hot solution of sulphate of potassa, or by boiling sulphate of potassa with sulphuric acid. The first crystals which form are in delicate needles of an acid taste, soluble in 2 parts of water at 60°, and consists of

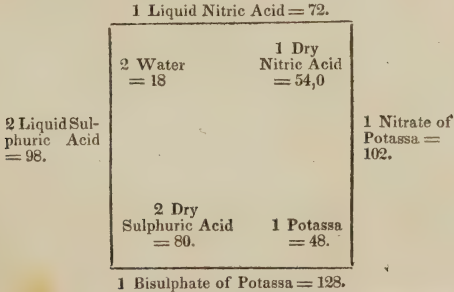
Bi-sulphate.

2 proportionals of acid = 80
1 ----- potassa = 48
128

Bi-sulphate of Potassa is also formed in the distillation of equal parts of nitre and sulphuric acid: nitric acid passes over, and a residuary bi-sulphate of potassa is produced, commonly known under the name of *sal enixum*. It is the *arcantum duplicatum*, or *panacea Holsatica* of old pharmacutists. It is used for cleansing coin and other works in metal; and has a place in the *London Pharmacopœia*.*

Sal enixum.

* The following diagram will illustrate the formation of this salt, and of liquid nitric acid, in the distillation of two proportionals of sulphuric acid with one of nitre:



Phosphuret of potassium is a brown compound, which rapidly decomposes water, producing

Carbonate of
potassa.

994. *Potassa and Carbonic Acid*.—The *carbonate* and the *bicarbonate* of potassa have been long used and known under various names—such as *fixed nitre*, *salt of tartar*, *salt of wormwood*, *vegetable alkali*, &c. Their composition was first ascertained by Black. Bergman, in 1774, described their most essential properties.*

995. *Carbonate of Potassa* is a salt of great importance in many arts and manufactures, and is known in commerce in different states of purity, under the names of *wood-ash*, *pot-ash*, and *pearl-ash*. It is the *subcarbonate of potassa* of the *U. S. Pharmacopœia*.

Exp.

The simplest mode of showing the absorption of carbonic acid by potassa, is the following: Fill a common phial with carbonic acid gas over water; and when full, stop it by applying the thumb. Then invert the bottle in a solution of pure potassa contained in a cup, and rather exceeding in quantity what is sufficient to fill the bottle. The solution will rise into the bottle, and if the gas be pure, will fill it entirely. Pour out the alkaline liquor, fill the bottle with water, and again displace it by the gas. Proceed as before, and repeat the process several times. It will be found, that the solution will condense many times its bulk of the gas; whereas water combines only with its own volume.

Exp.

This experiment may be made in a much more striking manner, over mercury, by passing into a jar, about three fourths filled with this gas, a comparatively small bulk of a solution of pure potassa, which will condense the whole of a large quantity of the gas. If dry hydrate of potassa be substituted in this experiment, no change will ensue; which proves that solution is essential to the action of alkalies on this gas. A solution of potassa, which has condensed all the carbonic acid it is capable of absorbing, when evaporated to dryness, affords *sub-carbonate*, or, more properly, *carbonate of potassa*.—H. 1. 541.

996. This salt is fusible without decomposition, at a red heat: it is very soluble in water, and deliquesces by exposure to air, forming a dense solution, once called *oil of tartar per deliquium*. Its taste is alkaline, and it renders vegetable blues

phosphuretted hydrogen gas, and hydrophosphuret of potassa. It is formed by cautiously heating potassium with phosphorus out of the contact of air.

Hypophosphite of Potassa has been examined by Dulong. It is very deliquescent, and soluble in water and alcohol nearly in all proportions. When heated it evolves phosphuretted hydrogen and phosphorus, and is converted into phosphate of potassa.†

Phosphite of Potassa is a soluble deliquescent uncrystallizable salt, not hitherto accurately examined.

Phosphate of Potassa may be obtained by neutralizing a solution of carbonate of potassa with phosphoric acid, concentrating the solution, and setting it aside for some days to crystallize.‡ It is a compound of 1 atom phosphoric acid, 1 atom potassa and 1 atom of water.

This phosphate has little taste. By the action of heat it undergoes the igneous fusion. The vegetable grains belonging to the *cerealia* contain a small quantity of the salt. H 1. 547.

Subphosphate of Potassa.—When phosphate of potassa is fused in a platinum crucible with potassa it is converted into subphosphate of potassa, which is insoluble in cold, and very difficultly soluble in hot water. It is fusible before the blow-pipe, yielding a globule, opaque when cold, but transparent whilst in fusion. The theoretical composition of this salt is

$$\begin{array}{rcl} 2 \text{ proportionals of potassa} & = & 96 \\ 1 \text{ ————— acid} & = & 28 \\ \hline & & 124 \end{array}$$

Superphosphate or Biphosphate of potassa is formed by dissolving the neutral phosphate in phosphoric acid and evaporating till crystals are obtained, which are prismatic and very soluble.

* *Opuscula*, vol. ii. p. 13.

† *Annales de Chim. et Phys.* ii. 142

‡ *T. First Principles*, ii. 256.

green. Its composition is differently stated by different chemists.

| | Acid. | Base. | Composition: |
|---|-------------|-------|--------------|
| According to Dalton 100 grs. consist of | 31,10 . . . | 68,9 | |
| ———— Dulong | 30,70 . . . | 69,30 | |
| ———— Dr Wollaston | 31,71 . . . | 68,29 | |

The proportions of 31,71 to 68,29 agree very nearly with the notion, that the carbonate of potassa is constituted of an atom of carbonic acid, weighing 22, and an atom of potassa weighing 48, and that the weight of its atom is 70. According to Mr Phillips the crystallized salt contains 2 atoms of water.*

The solution of carbonate of potassa will be found to have a much milder taste than the pure alkali, and no longer to destroy the texture of woollen cloth; but it still turns to green the blue infusion of vegetables.

997. For experimental purposes carbonate of potassa may be obtained from crystals of tartar (bi-tartrate of potassa) calcined in a crucible; then lixiviated with water, and evaporated to dryness. By this treatment the salt yields about one third its weight of dry carbonate. Or the tartar may be mixed with about an eighth of purified nitrate of potassa, and wrapped up in a paper in the form of cones, which may be placed on an iron dish, and set on fire. The residuary mass is to be lixiviated, and evaporated as before directed. Or purified nitrate of potassa may be mixed with a fourth of its weight of powdered charcoal, and projected into a red-hot crucible, the contents of which are to be poured, when in fusion, into an iron dish. The carbonate, thus obtained, amounts to rather less than one half the nitre which has been employed. Even when thus prepared, it is apt to contain some impurities, consisting chiefly of a minute proportion of sulphate and muriate of potassa, with a little silica, from which it is extremely difficult entirely to free it. That which is procured from burnt tartar may be made to crystallize, in which state it contains 20,60 per cent. of water.

How obtain-
ed.

998. The great consumption of this article in various manufactures is exclusively supplied by the combustion of vegetables, and consequently its production is almost limited to those countries which require clearing of timber, or where there are vast natural forests. The English market is chiefly supplied from North America. If any vegetable growing in a soil not impregnated with sea-salt be burned, its ashes will be found alkaline from the presence of carbonate of potassa. If the ashes be submitted to heat, so as to burn away the carbonaceous matter entirely, they become a white mass generally termed *pearl-ash*.

Sources of
potassa.

999. In the state of union with carbonic acid potassa generally occurs in the arts. The potash and pearlash of commerce are in fact *carbonates* of potassa of different degrees of purity. The quantity of carbonic acid, contained in these alkalies, may be

Method of de-
termining the
quantity of
carbonic
acid.

* *Philos. Mag.* N. S. 1469.

learned by a very simple experiment. Put one or two hundred grains of the alkali into a Florence flask, and add a few ounce-measures of water. Take also a phial filled with dilute sulphuric acid, and place this, as well as the flask, in one scale. Balance the two, by putting weights into the opposite scale, and, when the equilibrium is attained, pour gradually the acid into the flask of alkali, till an effervescence no longer ensues. When this has ceased, the scale containing the weights will be found to preponderate. This shows that the alkali, by combination with an acid, loses considerably of its weight; and the exact amount of the loss may be ascertained, by adding weights to the scale containing the flask and phial, till the balance is restored.

Of detecting
adulteration.

1000. Carbonate of potassa dissolves very readily in water, which, at the ordinary temperature, takes up more than its own weight.—Hence, when an alkali, which should consist almost entirely of carbonate of potassa, is adulterated, as very often happens, with substances of little solubility, the fraud may be detected by trying how much of one ounce will dissolve in two or three ounce measures of water. In this way may be detected an adulteration of one third its weight of sulphate of potassa. There are certain substances of ready solubility, however, which may be used in adulterating pearlshes, as common salt for example; and, when this is done, we must have recourse to an acid test for the means of discovery.*

Ure's¹ Alkali
meter.

* An instrument called an *Alkalimeter* is sometimes used, the following is the method of using that known as Dr Ure's—

Let a tube, closed at one end and of about three fourths of an inch internal diameter, and nine inches and a half in length, have 1000 grains of water weighed into it; then let the space it occupies be graduated into 100 equal parts, and every 10 divisions numbered from above downwards. At 23,44 parts, or 76,56 parts from the bottom, make an extra line a little on one side, or even on the opposite side to the graduation, and write at it with a scratching diamond *Soda*; lower down at 48,96 parts make another line, and write *potassa*; still lower at 54,63 parts, a third line, marked *carb. soda*; and at 65 parts a fourth, marked *carb. potass*. It will be observed that portions are measured off, beneath these marks, in the inverse order of the equivalent numbers of these substances, and consequently directly proportionate to the quantities of any particular acid, which will neutralize equal weights of the alkalies or their carbonates. The tube is now completed, except that it should be observed whether the aperture can be perfectly and securely covered by the thumb of the left hand, and if not, or if there be reason to think it not ultimately secure, then it should be heated and contracted until sufficiently small.

Diluted sulphuric acid must now be prepared to be used with the tube. When of a specific gravity of 1,127, it will be very nearly, if not accurately, of the strength required: and this may be obtained by mixing 19 parts of oil of vitriol of specific gravity 1,849, with 81 parts of water. If, when cold, the specific gravity of this diluted acid be as above mentioned 1,127, it must be nearly, if not exactly, of the strength required; but before being admitted into use, should be examined experimentally. Assuming it however as being absolutely correct, it will be found that a quantity measured into the tube up to any one of the four marks described, is sufficient to neutralize 100 grains of the dry alkali or carbonate set down at the mark; consequently if water be added in the tube, thus filled up to any one of the marks, until the 100 parts are full, and the whole uniformly mixed, one part of such diluted acid will neutralize one grain of the alkali or carbonate named at the mark, up to which the acid of specific gravity 1,127 was first filled.

When a specimen of potassa, or barilla, or kelp, is to be examined by this instrument, 100 grains are to be weighed out, dissolved in warm water, filtered, the insoluble portion washed, and the solution added to the rest; by this process the alkali will be separated from carbonate of lime, or other insoluble matters, which otherwise might cause errors in the estimation. The alkaline solution is to

1001. *Bi-carbonate of Potassa* is formed by passing a current of carbonic acid into a solution of the subcarbonate. By evaporation, crystals are obtained, the primary form of which is a right oblique-angled prism. Their taste is only slightly alkaline, and they require for solution four parts of water at 60°. Exposed to a red heat, carbonic acid is evolved, and carbonate of potassa remains. This bi-carbonate consists of

| | | |
|---|--------------------------------|------|
| 2 | proportionals of carbonic acid | = 44 |
| 1 | potassa, | = 48 |
| | | — |
| | | 92 |

Composition.

be put into a basin on the sand-bath, and then the tube and acid prepared. For this purpose some of the acid, of specific gravity 1.127, is to be poured into the tube until it rises up to the mark indicating the substance to be tested for; potassa or carbonate of potassa for the potash or pearlash of commerce, and soda or carbonate of soda for barilla or kelp: then water is to be added, until the hundred parts are filled, and closing the tube with the finger, its contents are to be perfectly agitated and mixed.

The alkali in the basin is now to be neutralized with the acid in the tube. After having once placed the thumb of the left hand over the aperture of the tube, it is not to be again removed; but inverting the tube by turning the hand so that the thumb and the mouth of the tube are downwards, the acid is to be let out gradually into the alkaline solution, by relaxing the thumb and admitting a succession of small bubbles of air; the hot solution beneath is to be continually stirred, so as to mix the acid instantly with the whole, and the operator must proceed with increased caution as the point of neutralization is approached. Very small quantities of the acid may be added, by slightly relaxing the thumb so as to permit a minute quantity, less than a drop, to flow to its extremity, and touching it with a glass rod; the final adjustment may thus be made more accurately, than by dropping the acid from the lip of the tube. The process must be thus carried on, until the alkali is found by the test papers to have been exactly neutralized: then the tube must be inverted, the thumb removed, drawing its under surface over the edge of the tube, so as to leave as much as possible of the fluid that otherwise might adhere to it, and having allowed the sides to drain, it must be observed how many parts of acid have been used, the number of which will indicate the number of grains of the alkali or carbonate, contained in the 100 grains of the impure alkali operated with.

With respect to the proper strength of the acid it is to be examined in the following manner: crystals of bi-carbonate of potassa are to be fused in a platinum crucible, the fluid poured out upon a clean, cold metal plate, and a piece of the resulting solid, estimated to be 70, 80, or 100 grains, weighed in water; in this way a known weight of pure carbonate of potassa will be obtained in solution. The solution is then to be diluted, heated, and neutralized by acid from the tube diluted as before described from the mark of carbonate of potassa. If it be found that as many parts of the acid have been used as of grains of the carbonate weighed out, the acid is of proper strength: if more acid has been used, it is too weak, if less has been sufficient, it is too strong. Suppose for instance that 100 grains of the salt (fused carbonate of potassa) had been used, and that 90 parts of the acid were sufficient; then these 90 parts ought to have occupied the 100, and consequently the 100 parts contain 1-10th too much acid, in consequence of the experimental acid itself containing 1-10th more than it ought to do. Hence the latter must be diluted with such a quantity of water as will make nine volumes in ten, or by 1-9th its volume; for as the 90 parts used are to the 100 parts they ought to have occupied, so is any number or parts by volume of the acid under trial, to the number of parts which it ought to occupy. The difference between the two last numbers will give the quantity of water in volumes, to be added to the acid expressed by the first of them, in order to correct it and make it of proper strength. On the contrary, if it were found that the 100 parts were insufficient, and that 110 parts more of similar acid were required, then there is too much water by 1-11th of the whole in bulk, which would be corrected by adding 1-10th of the 35 parts; hence 0.7 parts by weight of the same oil of vitriol that was used before, must be added for every 35 parts of the mixed acid. The correction in any other case may be easily made by considering that the number of parts over a hundred which are necessary to saturate the 100 grains of carbonate of potassa, are proportionate to the quantity of oil of vitriol which must be added to bring the experimental acid to proper strength: thus if 135 parts of the diluted acid were used, then 36-hundredths more of the weight of oil of vitriol already used must be added; and the quantity of oil of vitriol that was added at first being known to be 1-5th by weight, the additional quantity required is easily ascertained. These corrections are not strictly accurate, but sufficiently so to meet the exaggerated cases but of a difference of 10 parts, and to bring it within the limit of errors of experiment.—Faraday's *Chem. Manip.* Sect. xii.

For a table of the ingredients of the principal varieties of potash of commerce, see *Appendix*.

In its crystalline form it contains water equal to one proportional; and, therefore, consists of

92 carbonate
9 water

101

In the *London Pharmacopœia* the more expensive method of obtaining this salt by the action of carbonate of ammonia on carbonate of potassa is resorted to.

Preparation.

The following proportions may be used for the preparation of bi-carbonate of potassa upon the large scale; 100 lbs of purified carbonate of potassa are dissolved in 17 gallons of water, which, when saturated with carbonic acid, yields from 28 to 30 lbs of crystallized bi-carbonate; 50 lbs of carbonate of potassa are then added to the mother liquor, with a sufficient quantity of water to make up 17 gallons, and the operation is repeated.

Differs from the carbonate.

1002. The *Bi-carbonate of Potassa* differs from the carbonate in the following particulars:

In the greater mildness of its taste. Though still alkaline, yet it may be applied to the tongue, or taken into the stomach, without exciting any of that burning sensation, which is occasioned by the carbonate.

It is unchanged by exposure to the atmosphere.

It assumes the shape of regular crystals. The form of these crystals is a four sided prism, with dihedral triangular summits, the facets of which correspond with the solid angles of the prism.

Action of water,

It requires, for solution, four times its weight of water at 60°; and, while dissolving, absorbs caloric. Boiling water dissolves five-sixths of its weight; but, during this solution, the salt is partly decomposed, as is manifested by the escape of carbonic acid gas. The quantity thus separated amounts, according to Berthollet, to about $\frac{1}{10}$ th the weight of the salt. Dobereiner finds, also, that the crystals when dissolved in the smallest possible quantity of water, or when covered with water and left for half an hour in a vacuum, lose one fourth of their acid.

of heat.

By calcination in a low red heat, the portion of carbonic acid, which imparts to the salt its characteristic properties, and all the water are expelled, and the salt returns to the state of carbonate.*

Decomposed by acids.

1003. Bi-carbonate of potassa, in all its forms, is decomposed by the stronger acids; as the sulphuric, nitric, and muriatic, which unite with the alkali, and set the gas at liberty. This may be shown by pouring on the carbonate, contained in a gas bottle, any of the acids, and collecting the gas by a proper apparatus. H. 1. 546.

Cyanide.

1004. *Cyanide of Potassium*.—Potassium heated in cyanogen absorbs the gas, and produces a grey *cyanide of potassium*, which by the action of water becomes *hydrocyanate of potassa*. This salt speedily decomposes, and becomes converted into carbonic acid and ammonia.

* This is the best method of obtaining pure carbonate of potassa for chemical purposes.

1005. *Hydro-cyanate of Potassa* may be formed by the mixture of hydro-cyanic acid, and liquid hydrate of potassa. Hydro-cyanate. It is very soluble, is alkaline to the taste, and turns syrup of violets green; it is decomposed by the weaker acids, even by the carbonic. With salts having protoxide of iron for a base, it gives a precipitate which is at first orange coloured, and afterwards, by exposure to the air, changes to green and to deep blue. From solutions containing peroxide of iron, it causes a pale blue precipitate, the colour of which becomes deeper by exposure to air.

1006. *Ferro-cyanate of Potassa*.—When the salt just described is digested in a state of solution with protoxide of iron, a portion of the oxide is dissolved, the solution becomes yellow, and on adding more hydro-cyanic acid is rendered neutral, crystallizable, and capable of resisting decomposition by weak acids. But the same compound may be better formed by digesting Prussian blue in fine powder with liquid hydrate of potassa. The common Prussian blue of commerce should first be heated with an equal weight of sulphuric acid, (diluted with five or six parts of water) and then be washed with a large quantity of distilled water. This will remove the alumina which it always contains. After being thus purified, it may be added to the hydrate of potassa, as long as that liquor continues alkaline. The filtered liquor, when evaporated and cooled, deposits crystals, which are quadrangular prisms. These may be purified by a second crystallization. Ferro-cyanate.

1007. The ferro-cyanate (formerly called triple prussiate) of potassa is a transparent salt, often in fine large crystals, of a lemon yellow colour.* It is free from taste and smell. Specific gravity 1,833. Water at 60° F. dissolves nearly one third of its weight, and boiling water nearly an equal weight of the salt. When heated, it loses 13 per cent. and becomes white, but does not run into fusion, or undergo decomposition. Submitted to a still higher temperature in a retort, it is decomposed, and yields hydro-cyanic acid and ammonia, besides carbonic acid, carbonic oxide and carburetted hydrogen; and a residue is left, composed of charcoal, metallic iron, and potassa, which last is still united with more or less cyanogen.† Properties.

1008. Diluted acids have little action on ferro-cyanate of potassa, except with the aid of heat, and then the sulphuric, muriatic and even the acetic disengage a certain quantity of hydrocyanic acid, and occasion a white precipitate, the nature of which is not understood. Red oxide of mercury digested with a solution of the salt, decomposes it, and gives rise to the formation of cyanide of mercury, and to the disengagement of free alkali, and of peroxide of iron attached to a little acid. Action of acids.

* The mathematical form has been described by Mr Brooke in *Ann. Philos.* N. S. vi. 41, and by Mr Levy in *Quart. Jour.* xv. 288.

† See Robiquet in *Ann. de Chim. et de Phys.* xvii. 205.

1009. The solution of ferro-cyanate of potassa is not precipitated by alkalies, or by alkaline salts, but is decomposed by some of the earthy, and by almost all the metallic salts.*

Analysis:

1010. The ferro-cyanate of potassa has been analyzed by Berzelius, who decomposed it by heating it with peroxide of copper, and obtained carbonic acid and azotic gases, in the proportions in which they are evolved by the decomposition of cyanogen, viz. 2 volumes of the former and one of the latter. Hence he considers it as a cyanide, and not a prussiate, and deduces its composition to be two atoms of cyanide of potassium + 1 atom of cyanide of iron. According to Mr Porrett its composition is

| | Atoms. | | Atoms. |
|---------|-------------------------|----------|-------------|
| Potassa | 40,34 . . 1 | Azote | 11,76 . . 1 |
| Iron | 11,76 . . $\frac{1}{2}$ | Hydrogen | ,84 . . 1 |
| Carbon | 20,17 . . 4 | Water | 15,13 . . 2 |

—forming 1 atom of ferro-cyanic acid. H. 1. 553.†

Sulphocyanate of potassa,

1011. *Sulphocyanate of potassa* is prepared by heating the ferrocyanate with sulphur, a process first proposed by Grotthus, and since modified by M. Vogel and Dr Turner. The most convenient method is to mix the ferro-cyanate, in fine powder, with an equal weight of sulphur, and to place the mixture, contained in a porcelain capsule, just above a pan of burning charcoal, so that it may be exposed to a very strong heat, but short of redness. The mixture is speedily fused, takes fire and burns briskly for one or two minutes, during which it should be well stirred. The combustion then ceases spontaneously, and the dark coloured residue, consisting of unburned sulphur, sulphocyanuret of potassium, and sulphuret of iron, on being dissolved in water and filtered, yields a very pure and neutral sulpho-cyanate of potassa. To insure the decomposition of all the ferro-cyanate of potassa, the mass may be allowed to remain in a fused condition for a few minutes after the combustion has ceased, previous to withdrawing it from the fire.

how obtained.

Theory:

1012. In this process the iron and cyanogen of the ferro-cyanate combine with separate portions of sulphur, forming a sulphuret of iron and a sulphuret of cyanogen, the latter of which unites with potassium. On the addition of water, a portion of that liquid is decomposed, and the sulphocyanate of potassa is generated.

Composition.

1013. The sulphocyanate of potassa contains one atom of the acid and one atom of the oxide. The salt exists only in a liquid state for the crystals which are deposited from a concentrated solution, when separated from the adhering moisture by bibulous paper do not contain either water or its elements, but are a pure sulphocyanuret of potassium. The crystals are very deliquescent on exposure to the air, and dissolve freely in water,

* For a table of the colours of precipitates from various solutions, both by the ferro-cyanate and hydro cyanate of potassa, see *Appendix*.

† According to Mr Phillips, (*Phil. Mag. N. S.* 1. 110) it is composed of 6 atoms carbon, 3 azote, 3 hydrogen, 1 oxygen and 1 iron forming 1 atom of ferro-cyanic acid; and 2 atoms potassa.

yielding a solution which is quite neutral. In form, taste and fusibility, they are very analogous to nitre.

1014. The sulphocyanate of potassa is employed in preparing the sulphocyanic acid, and as a test for detecting the presence of the peroxide of iron.* Uses.

1015. *Sub-borate of potassa* is a salt which has been scarcely examined; it may be formed by the direct combination of liquid hydrate of potassa with boracic acid, or by exposing a mixture of boracic acid and nitre to a bright red heat.† Sub-borate.

1016. The salts of potassium are soluble in water, and afford no precipitates with pure or carbonated alkalies. They produce a precipitate in muriate of platinum, which is a triple compound of potassa, oxide of platinum, and muriatic acid. They are not changed by sulphuretted hydrogen, nor by ferro-prussiate of potassa. Added to sulphate of alumina, they enable it to crystallize, so as to form alum. Properties of the salts of potassium.

1017. *Alloys of Potassium*.—Potassium combines with several of the metals, forming alloys which are decomposed by water, its oxygen uniting with the potassium and forming potassa, while its hydrogen is disengaged and the other metal precipitated. Several of these alloys have been described by M. Serullas in the *Annales de Chimie et Physique*.‡ An alloy of potassium and antimony may be obtained by the following process. Alloys.

One hundred grains of emetic tartar (*antimonium tartarizatum U. S. Pharmacopœia*) are to be mixed, by careful rubbing, with 3 grains of lamp-black or common charcoal. Select crucibles holding 75 or 80 grains, which must not be more than three quarters filled, make the upper edge smooth, and rub the whole inside with charcoal powder, that the mixture may not adhere to the sides. The materials are to be placed in the crucible, and covered with charcoal powder; the cover is then to be carefully luted on. Place the crucible in a furnace and expose it to a bright red heat for three hours, then set it by for *six hours* to cool. This time is required to allow the air, which always penetrates more or less into the crucible, to burn the exterior layer of the mass; if withdrawn too soon from the fire it always explodes spontaneously. After it has been cooled, the cover of the crucible may be removed, and the calcined mass should, without loss of time, and without breaking up, be introduced into a wide mouthed bottle which should be carefully closed with a ground stopper. The mass gradually splits into fragments of different sizes, and in this state will preserve its properties for years.§

1018. When this alloy has been well prepared it is extremely fulminating, so as to detonate with a report like fire-arms, by the first contact of water. Detonation with water.

1019. With this substance gun-powder may be fired under water. The experiment was made in the following manner: Inflames gun-powder under water.

Half an ounce of gun-powder was put into a strong glass tube closed at one end, of which the powder filled about one quarter. A piece of the fulminating Exp.

* Turner.

† Selenic acid is capable of uniting with potassa in three different proportions, and of composing either a seleniate, biseleniate, or quadriseleniate, but these salts are not of much importance—See Berzelius's paper in *Ann. de Chim. et de Phys.* ix. 257.

‡ See also *Boston Journal of Philos.* ii. 61.

§ This alloy may also be obtained by heating equal parts of potassa and metallic antimony.—*Amer. Jour. of Science*, &c.

alloy of the size of a pea, was laid upon the powder. The tube was immediately closed with a cork which had been previously perforated with a small hole, stopped for the present with a little fat lute, soft enough to be readily pierced with a sharp pin when required. The tube thus prepared, was then sunk in a large vessel of water two or three feet deep, and was confined by weights to the bottom. The lute stopping the perforation in the cork was then pierced with a steel wire fixed to the end of a long stick, and the moment that the water entered the tube the powder exploded, breaking the tube, and throwing out a four pound weight which had fixed it down.

Other alloys.

1020. Several triple alloys of potassium and other metals have also been described by M. Serullas, which may be formed by the processes described below.*

SECTION III. Sodium.

Discovery of sodium.

1021. Sodium discovered by Sir H. Davy in 1808, is obtained from soda by an operation analogous to that for procuring potassium from potassa. (952). It is soft, easily sectile, white and opaque, and when examined under a thin film of naphtha has the lustre and general appearance of silver.

Properties.

1022. It is exceedingly malleable, and much softer than any of the common metallic substances. When pressed upon by a

Potassium, copper and antimony.

* *Alloy of Potassium, Copper and Antimony.* This is obtained by melting together equal parts of carbonized tartar (prepared by roasting *cream of tartar* of commerce in an open crucible, till it has lost about half its weight) regulus of antimony, and copper filings. The carbonized tartar and antimony should be first rubbed together, and then placed in a crucible, the copper filings being laid above them.† The cover of the crucible being luted on, the whole is to be strongly heated for two hours. This alloy has a violet tint, it divides into very thin brilliant laminae, which flatten a little under the hammer. It is volatile in the fire, and pieces thrown upon mercury, covered with a little water, turn round rapidly.

Of potassium, silver and antimony.

Alloy of Potassium, Silver and Antimony, is prepared like the last; it is more volatile; its colour steel grey, and it has much lustre. It is very brittle, and contains much potassium.

Potassium, iron and antimony.

Alloy of Potassium, Iron and Antimony, is obtained by putting at the bottom of a crucible some iron turnings, broken to small fragments; covering them with equal parts of calcined tartar and antimony, previously mixed, and exposing to a very strong heat.

Potassium and bismuth.

Alloy of Potassium and Bismuth. Rub together 60 grains of calcined tartar, 120 of bismuth and one of nitre, enclose the mixture in a crucible, covered with lamp black, close it carefully and heat it for two hours. An alloy is obtained which is very rich in potassium, its smallest fragments giving sparks when cut with shears. As soon as it is broken, it melts and burns, leaving a residue of a greenish oxide.‡

If this alloy is made with 10 or 12 grains of lamp-black or charcoal instead of the nitre, a pyrophorus is obtained, which takes fire by the contact of water, and burns with slight explosions. It may be used for kindling gun powder under water.

Potassium and tin.

An *alloy of Potassium and Tin* is made in the same manner as the preceding, with 100 parts of oxide of tin, 60 of calcined tartar and 10 of lamp-black. A double dose of lamp-black gives a pyrophorus.

Potassium and lead.

An *alloy of Potassium and Lead* is produced by 100 grains of protoxide of lead and 60 of calcined tartar; and an addition of 5 or 6 grains of lamp-black gives a pyrophorus.

M. Serullas remarks that in the preparation of these alloys, the stratum of charcoal put over them to protect them from the action of the air, though in no way mixed with them, acquires the property of spontaneous inflammation in the air; which he conceives can only be attributed to the presence of potassium volatilized during the fusion, and retained by the charcoal.

† The copper filings should be previously mixed with a sixth part of antimony to promote their fusion.

‡ In certain cases this alloy offers an excellent test of the complete desiccation of gas. All that is required is to pass up a small fragment of the alloy to the gas confined over mercury, when the least moisture will cause it to turn round. (S.)

platinum blade with a small force, it spreads into thin leaves; and a globule of $\frac{1}{10}$ th or $\frac{1}{2}$ th of an inch in diameter is easily spread over a surface of a quarter of an inch. This property is not diminished by cooling it to 32° Fahrenheit. Several globules, also, may, by strong pressure, be forced into one; so that the property of *welding*, which belongs to platinum and iron at a high degree of heat only, is possessed by this substance at common temperatures.

It is lighter than water; as near as can be determined, its specific gravity is as 0.972 to 1.

1023. It is much less fusible than the base of potassa. At 120° Fahrenheit, it begins to lose its cohesion, and is a perfect fluid at 180° or 190° . Hence it readily fuses under heated naphtha.

1024. When sodium is exposed to the atmosphere, it immediately tarnishes, and by degrees becomes covered with a white crust of soda, which deliquiates more slowly than that formed on potassium. It is not changed, however, by air that has been artificially dried. Effect of air.

1025. It combines with oxygen, slowly and without luminous appearance, at all common temperatures. When heated to its fusing point, the combination becomes more rapid; but no light is emitted till it becomes nearly red hot. The flame which it then produces, is white, and it sends forth bright sparks, exhibiting a very beautiful effect. In common air, it burns with a similar colour to charcoal, but with much greater splendour. Of oxygen.

1026. When thrown into water, it produces a violent effervescence and a loud hissing noise; it combines with the oxygen of the water to form soda; and hydrogen gas is evolved, which does not, however, as in the case of potassium, hold any of the alkaline base in solution. Neither can sodium be made to dissolve in hydrogen gas, by being heated in contact with it. When thrown into hot water, the decomposition is more violent, and in this case a few scintillations are generally observed at the surface of the fluid; but this is owing to small particles of the base, which are ejected from the water, sufficiently heated to burn in the atmosphere. Action on water.

1027. Its action on alcohol, ether, volatile oil, and acids, is similar to that of potassium; but with nitric acid a vivid inflammation is produced. H. 1. 557. On alcohol.

1028. *Sodium and Oxygen*.—From the quantity of hydrogen evolved when sodium is thrown into water, we learn that soda (*protoxide of sodium*) consists of about 75 sodium and 25 oxygen *per cent.*; and if it be considered as the protoxide, the number representing the metal will be 24, and *soda* will consist of 24 S. + 8 O. and be represented by 32. Soda.

1029. The peroxide of sodium may be formed, by burning the metal with an excess of oxygen. It is of a deep orange colour, very fusible, and a nonconductor of electricity. When acted on by water, its excess of oxygen escapes, and it becomes Peroxide.

soda. It deflagrates with most combustible bodies. It appears to be constituted of 2 atoms of sodium = 48, with 3 atoms of oxygen = 24, and its equivalent number is therefore 72.

Soda, how obtained.

1030. *Soda*, as it usually occurs in the laboratories, is obtained from the carbonate, by the action of lime and alcohol, as described under the head *potassa*. It may also be formed by burning sodium in a quantity of air, containing just oxygen enough to convert the metal into alkali. It is of a grey colour; of a vitreous fracture; and requires a strong red heat for its fusion. It consists of 32 protoxide of sodium + 9 water, and is represented by 41. When soda is exposed to air, it soon becomes covered with an efflorescence of carbonate of soda.

Distinguish-
ed from po-
tassa.

1031. Soda is distinguished from potassa, by forming an *efflorescent* paste when exposed to the atmosphere; potassa under the same circumstances *deliquesces*. If excess of tartaric acid be added to a solution of soda there is no precipitation; but in solution of potassa it occasions a deposit of minute crystals. Solution of soda occasions no precipitate when added to solution of muriate of platinum. Solution of potassa occasions a yellow precipitate in solution of platinum. In combination with acids it produces a perfectly distinct class of salts.

Chloride.

1032. *Chloride of Sodium*.—Sodium, when heated in chlorine, burns and produces a white compound, of a pure saline flavour, soluble in $2\frac{1}{2}$ parts of water at 60° , and forming cubical crystals. It may also be formed by heating sodium strongly in muriatic acid gas; the hydrogen of which is liberated, while the chlorine combines with the metal.

How obtain-
ed.

1033. Or it may be formed by saturating carbonate or hydrate of soda with muriatic acid, and evaporating the liquid, which yields chloride of sodium in a solid form. This chloride also, is an abundant product of nature, being that well known substance, common salt. For purposes of experiment, the common salt may be employed, which is to be found in the shops. This may be purified, by adding to a solution of it in water a solution of carbonate of soda, as long as any milkiness ensues; filtering the solution, and evaporating it till it crystallizes.

Properties;

1034. It crystallizes in solid regular cubes, or, by hasty evaporation, in hollow quadrangular pyramids, which, when the salt is pure, are but little changed by exposure to the air. The common salt of the shops, however, being impure, acquires an increase of weight, in consequence of the absorption of moisture. The various forms under which it appears, of stoved salt, fishery salt, bay salt, &c. arise from modifications in the size and compactness of the grain, rather than from any essential difference of chemical composition.

1035. It requires for solution, twice and a half its weight of water, at 60° Fahrenheit, and hot water takes up very little more. Hence its solution crystallizes, not like that of nitre, by cooling, but by evaporation. When heated gradually, it fuses, and forms, when cold, a solid compact mass. If suddenly heat-

ed as by throwing it on red-hot coals, it decrepitates. It does not, however, after being dried at the temperature of boiling water, lose by ignition more than two or three parts of water *per cent.* and essentially it contains no water. When mixed with powdered charcoal or sulphur, and fused in a crucible, it does not undergo any decomposition or essential change.

1036. It is decomposed by the carbonate of potassa, the alkali of which combines with the muriatic acid of the salt, and the carbonic acid is transferred to the soda.—Hence we obtain muriate of potassa and carbonate of soda.*

Decomposition.

1037. When chloride of sodium is dissolved in water, it passes, by the decomposition of that fluid, to the state of muriate of soda, and it is this salt and not the chloride of sodium (which last can only exist in a solid form) that is the ingredient of sea water and other solutions of common salt. Muriate of soda is composed, in 100 grains.

Action of water.

| | | | | Acid. | Base. | Composition. |
|--------------|-----|----|-----|-------|-------|------------------|
| According to | | | | | | |
| Darcet | . . | of | . . | 49,27 | . . | 50,73 |
| Berard | . . | " | . . | 43, | . . | 57, |
| Dr Marcet | . . | " | . . | 46, | . . | 54, |
| Berzelius | . . | " | . . | 46,56 | . . | 53,44 H. 1. 560. |

Chloride of sodium, as it exists in fused common salt, is constituted of an atom of sodium, weighing 24, with an atom of chlorine weighing 36, and its equivalent is 60.

Dr Wollaston assumes its constitution to be 39,64 sodium + 60,36 chlorine.

1038. In the common process for obtaining muriatic acid it is decomposed by sulphuric acid. In this decomposition there is a transfer of the oxygen contained in the water of the sulphuric acid to the sodium of the salt, the chlorine of which combines with the hydrogen of the water to produce muriatic acid gas. The oxide of sodium unites with the dry sulphuric acid to produce sulphate of soda.†

Action of sulphuric acid.

1039. *Chlorate of Soda* was procured by Mr Chenevix‡ by the same process as chlorate of potassa, but not possessing less solubility than chloride of sodium, the two substances are difficultly separable. Vauquelin obtained it by saturating chloric acid with soda. Its crystals resemble those of chlorate of potassa, its taste is also nearly similar.§||¶

Chlorate.

* A process for effecting this decomposition, on a large scale, is described by Westrumb, in *Crell's Journal*, English translation. ii. 127.

† Glauber first obtained muriatic acid from common salt, and the existence of soda in it was first shown by Duhamel.

‡ *Phil. Trans.* 1802.

§ *Bromine and Soda*, (339).

|| The combinations of chlorine with lime and with soda, have lately been highly recommended as disinfecting agents.

The *disinfecting soda liquid* of M. Labarraque is prepared by the following process. Dissolve 2800 grains of crystallized carbonate of soda in 1,28 pints of water, having placed the solution in a Woulfes' apparatus, pass through it a current of chlorine gas evolved from a mixture of 967 grains of salt, and 750 of oxide of manganese, acted upon by 967 grains of oil of vitriol previously diluted with 750 grains of water. The operation should be conducted slowly.

For most purposes the common *bleaching powder* sprinkled about or dissolved in water is quite as effectual and more economical, but for medical uses the preparation should be more nicely attended to. See *Quart. Jour. of Science, &c.* N. S. i. 236—ii. 460—iii. 84; and *Amer. Jour. &c.* xiv. 251.

¶ *Sodium and Iodine* act upon each other with the same phenomena as potassium, and an iodide of

Nitrate.

1040. *Nitrate of Soda* crystallizes in rhombs, soluble in three parts of water at 60° , and in less than its weight at 212° . It has a cool sharp flavour, and is somewhat deliquescent. It consists of 1 atom soda + 1 nitric acid. It is often found in crude nitre, resulting apparently from the decomposition of common salt; it is the *cubic nitre* of old writers. It may be formed by saturating carbonate of soda with nitric acid, or by distilling common salt with three-fourths its weight of nitric acid. When the former process is adopted, the solution must be evaporated, till a pellicle appears on its surface, and then allowed to cool.

Uses.

1041. The only use of nitrate of soda is, perhaps, that which has been suggested by Proust, who has found it to be more economical in the making of fire works than nitrate of potassa.*†† H. 1. 563.

Sulphate.

1042. *Sulphate of Soda—Glauber's Salt—Sal mirabile*—is abundantly produced in the manufacture of muriatic acid, by the action of sulphuric acid upon common salt.

Composition.

1043. Common salt consists of 24 sodium + 36 chlorine. Sulphuric acid consists of 40 dry acid + 9 water. The water of the acid, consisting of 1 hydrogen + 8 oxygen, is decomposed. Its hydrogen is transferred to the chlorine to produce gaseous muriatic acid (1 H. + 36 C. = 37 Mur. A.), and its oxygen unites to the sodium, forming dry soda (8 Ox. + 24 S. = 32 soda). The 40 dry acid, unite to the 32 soda, to produce sulphate of soda, which will be represented by the number 72.

1044. Sulphate of soda crystallizes from its aqueous solution in large four-sided prisms, transparent, and efflorescent, when exposed to air. The primary form is an oblique rhombic prism. They consist of 72 dry sulphate + 90 water; exposed to dry air the crystals part with about 50 per cent. of water.

Properties.

The taste of sulphate of soda is saline and bitter: it is soluble in rather less than three times its weight of water at 60° . When exposed to heat it undergoes watery fusion, that is, it melts in its own water of crystallization; when this has evaporated it fuses.

Decomposed
by chalk.

1045. Sulphate of soda is sometimes decomposed for the purpose of obtaining soda, by igniting it with chalk and charcoal,

sodium is obtained. The hydriodic acid and soda produce a similar compound. It is deliquescent, and its solution yields quadrangular crystals.

Iodate.

Iodate of Soda is made by dissolving iodine in solution of soda; a white compound forms, which is the iodate with a portion of hydriodate of soda; the latter may be removed by alcohol. Iodate of soda forms small prismatic tufted crystals, which when heated, afford oxygen and iodide of sodium—Gay Lussac, *Annales de Chimie*, xci.

* Nicholson's *Journal*, xv. 262. See also 6 *Ann. de Chim. et Phys.* 206.

† *Sulphuret of Sodium and of Soda*. See *Potassium*. (991). The sulphurets exhibit nearly similar properties.

‡ *Hyposulphite of Soda* is formed as hyposulphite of potassa. (995). It is difficultly crystallizable, deliquescent, of an intensely bitter taste, and insoluble in alcohol. Its aqueous solution readily dissolves moist chloride of silver.

Sulphite of Soda is crystallizable in transparent four and six-sided prisms, soluble in four parts of water at 60° . It consists of 32 soda + 32 sulphurous acid. The crystals contain eight proportionals of water. By exposure to the air, it effloresces and is changed into a sulphate.

or with iron and charcoal. (Of these processes a full account is given in AIKIN'S *Dictionary*, Art. *Muriate of Soda*.) Its principal use is in Pharmacy.*†

1046. *Phosphate of Soda* is usually obtained for pharmaceutical purposes by saturating the impure phosphoric acid, obtained from calcined bones by sulphuric acid,‡ with carbonate of soda: the liquor is filtered, evaporated, and set aside to crystallize. The primary form of the crystals is an oblique rhombic prism. It was introduced into pharmacy by Dr Pearson; it is the *sal perlatum* of some old writers. Phosphate.

1047. This salt has a pure saline taste and when dry is constituted, according to Berzelius, of phosphoric acid 53,48, soda 46,52. Dr Thomson states the anhydrous salt to consist of acid 46,67, soda 53,33 or 1 atom of each, and the crystals generally to contain 12 atoms of water. Mr Dalton considers this as the bi-phosphate constituted of 2 atoms of acid and 1 of base. To render it neutral to colour-tests he finds that the acid must be doubled, or that the neutral phosphate is in fact a *quadriphosphate*. The simple phosphate, consisting of 1 atom of acid and 1 of base may be formed by adding as much more caustic soda to the biphosphate as it already contains. The new salt is much more soluble than the bi-phosphate and crystallizes in very fine needles. This Mr Dalton recommends as the proper reagent in chemical analysis.§ H. 1. 568. Composition.

When heated, phosphate of soda fuses and boils up, and having lost its water of crystallization, it runs into a clear glass, which becomes opaque on cooling. If a globule be heated before the blow-pipe it assumes the dodecaëdral figure as it cools. Action of heat,

1048. Treated with sulphuric acid, phosphate of soda is only partly decomposed, a *bi-phosphate of Soda* being formed, which is more soluble than, and not so easily crystallizable as the phosphate. of sulphuric acid.

1049. *Ammonio-phosphate of Soda* exists in human urine, whence it was procured by the early chemists under the names of *microcosmic* and *fusible salt*. When exposed to heat the ammonia is expelled, and a *bi-phosphate of soda* remains: it Ammonio-phosphate.

* *Bi-sulphate of Soda* is obtained by adding sulphuric acid to a hot solution of sulphate of soda. It crystallizes in rhomboids soluble in twice their weight of water at 60°. This salt consists of 72 sulphate of soda + 40 sulphuric acid = 112. Crell's *Annals*, 1796.

Ammonio-sulphate of Soda is a triple salt, formed by saturating the bi-sulphate with ammonia. Crell's *Annals*, 1796, 1.

Phosphite of Soda has not been examined. *Hypophosphite of Soda* is very soluble both in alcohol and water.—*Annales de Chim. et Phys.* ii. 142.

† If a drop of a solution of sulphate of soda be placed upon a glass plate and allowed to evaporate spontaneously, it will leave crystals which may be distinguished by their form and ultimate efflorescence, as the *anhydrous sulphate*. Most of the potassa and soda salts may be distinguished as to their base by such an experiment. They are easily converted into sulphates by a drop or two of sulphuric acid and ignition, and then, being dissolved and tried as above, will yield crystals which may be known by their forms, and more especially by their efflorescence if of soda, and their unchangeable state if of potassa. This test is, however, liable in certain circumstances to uncertainty. Faraday in *Quart. Jour.* N. S. v. 223.

‡ See *Phosphorus*.

§ *Manch. Memoirs*, N. S. iii. xi.

appears to consist of two proportionals of phosphoric acid = 56; one of soda = 32, and one of ammonia = 17.*

Carbonate, 1050. *Carbonate of Soda* is chiefly obtained by the combustion of marine plants, the ashes of which afford, by lixiviation, the impure alkali called *soda*. Two kinds of rough soda occur **sources of.** in the market; *barilla*, and *kelp*; besides which, some *native carbonate of soda* is also imported. Barilla is the semifused ash of the *salsola soda*, which is largely cultivated upon the Mediterranean shore of Spain, in the vicinity of Alicant. Kelp consists of the ashes of sea weeds, which are collected upon the sea coast and burned in kilns, or merely in excavations made in the ground and surrounded by stones. It seldom contains more than 5 per cent. of carbonated alkali, and about 24 tons of sea weed are required to produce one ton of kelp. The best produce is from the hardest *fuci*, such as the *serratus*, *digitatus*, *nodosus*, and *vesiculosus*.† The rough alkali is contaminated by common salt, and impurities, from which it may be separated by solution in a small portion of water, filtrating the solution, and evaporating it at a low heat: the common salt may be skimmed off as its crystals form upon the surface.

To obtain pure.

1051. When required of great purity, it is best prepared either from pure acetate of soda, which is decomposed at a red heat, and converted into carbonate of soda and charcoal, the former of which is separable by water; or it may be obtained by calcining the bi-carbonate. H.

Form and composition.

1052. The primitive crystalline form of carbonate of soda is an oblique rhombic prism.‡ It is soluble in twice its weight of water at 70°. Its taste is strongly alkaline, and it greens vegetable blues. It consist of

| |
|------------------|
| 32 soda |
| 22 carbonic acid |
| 54 |

Its crystals contain ten proportionals of water = 90 which may be expelled by heat. They effloresce by exposure to air. This salt is the *Sodæ-Subcarbonas* of the *Pharmacopœia*.§

Bi-carbonate.

1053. *Bi-carbonate of Soda* is formed by passing carbonic acid through the solution of the sub-carbonate. By evaporation a crystalline mass is obtained. This salt consists of

| |
|------------------|
| 32 soda |
| 44 carbonic acid |
| 76 |

The bi-carbonate of soda has a very slightly alkaline taste, and it is much less soluble in water than the sub-carbonate.

how obtained.

1054. This salt, as well as the bi-carbonate of potassa, may be obtained by treating their respective carbonates with carbonate

* Fourcroy, *Ann. de Chim.* vii. 183.

† Mac Culloch's *Western Islands*, vol. i. p. 122.

‡ Brooke *Ann. Philos.* N. S. vi. 287.

§ In the analysis of barilla and kelp, to ascertain the relative proportion of soda, it may be useful to know that 100 parts of dilute nitric acid, specific gravity 1.36, will saturate 50 parts of dry carbonate of soda, which are equivalent to about 29 of pure soda.

of ammonia; pure ammonia is evolved and bi-carbonates are formed.*

In the manufacture of this bi-carbonate for the purpose of commerce, 160 lbs. of carbonate may be dissolved in 13 gallons of water, and carbonic acid thrown into the solution in a proper apparatus. The bi-carbonate falls as it forms to the amount of about 50 lbs., and being separated from the solution may be conveniently dried by pressure in an hydraulic press, and subsequent exposure to heat not exceeding 100°. A fresh portion of carbonate is dissolved in the mother liquor, and the operation repeated as before.

Process for obtaining it in the large way.

1055. A mixture of the carbonates of soda occurs native in great abundance in Africa, in the province of Gahena, near Fezzan. The natives call it *Trona*. It has been analyzed by Mr R. Phillips, who considers it as a compound intermediate between the carbonate and bi-carbonate. Or to be constituted of 3 atoms of acid + 2 of soda, or of $1\frac{1}{2}$ atoms of acid = 33 + 1 of soda = 32, together 65. Hence he has given it the name of *sesqui-carbonate of soda*.†

Native.

Composition.

1056. The salt sold as bi-carbonate he finds to be a compound of an atom of carbonate and an atom of bi-carbonate, or to consist of carbonic acid 3 atoms, soda 2 atoms, water 4 atoms. The bi-carbonate of the shops is, therefore, a sesqui-carbonate combined with water. H.

A very productive soda-lake exists in South America in Maracaybo, one of the provinces of Venezuela.‡

1057. *Sub-borate of Soda—Borax*.—This salt, which has been very long known, is imported from India in an impure state, under the name of *Tincal*, which, when purified, is called *refined Borax*. It crystallizes in irregular hexaëdral prisms, slightly efflorescent. Its taste is alkaline and styptic. It is soluble in 20 parts of water at 60°, and in six parts of boiling water. When heated it loses water of crystallization, and becomes a porous friable mass, called *calcined borax*, or *glass of borax*. It consists, according to Gmelin, of

Borax.

35,6 acid
17,8 soda
46,6 water

Composition.

100,04

According to Thomson|| of 31,5 acid, 20,4 soda, 48, water, or of 2 atoms boracic acid, 1 atom soda and 8 atoms water. Under this view it is a *bi-borate*.

Sulphuric acid decomposes this salt, producing sulphate of soda and boracic acid. (824). It has a place in the *Pharmacopœia*, and is much used in experiments with the blow-pipe.¶

Action of sulphuric acid.

* See U. S. Pharmacopœia, p. 198. Bigelow's *Sequel*, p. 342. † *Jour. of Science*, &c. vii. 298.

‡ *Quarterly Journal*, i. p. 188. § *Ann. Philos.* vol. 9.

¶ *First Prin.* i. 167.

¶ *Seleniate of Soda*. Selenic acid unites with soda in three different proportions, but these salts have no particularly interesting properties.

Hydro-cyanate of Soda, like all the other salts of this class, is alkaline, and is decomposed by mere exposure to the atmosphere.

Ferro-cyanate.

1058. *Ferro-cyanate of Soda* is of a yellow colour, and forms four sided prisms, terminated by dihedral summits, which effloresce in the air, and lose $37\frac{1}{2}$ per cent. of their weight. At 55° F. they dissolve in $4\frac{1}{2}$ times their weight of water, but require much less boiling water, from which they separate on cooling. They are soluble in alcohol. H. F. 571.

Salts of sodium characterized.

1059. The salts of sodium are soluble in water. They are not precipitated either by pure or carbonated alkalies, or hydro-sulphuret of ammonia, or ferro-cyanate of potassa; they produce no precipitate in solution of muriate of platinum, and do not convert sulphate of alumina into octoëdral alum. Before the blow-pipe they tinge the flame yellow and increase its magnitude.

1060. Potassium and sodium form an alloy, which, if composed of one part of potassium and three of sodium, remains fluid at 32° . Equal parts of the metals form a brittle crystallizable alloy.

SECTION IV. *Lithium.*

Discovery.

1061. In the year 1818 in the analysis of a mineral, called petalite, M. Arfwedson discovered about three per cent. of an alkaline substance, which was at first supposed to be soda; but, finding that it required for its neutralization a much larger quantity of acid than soda, he was led to doubt its identity with that alkali, and the further prosecution of his inquiries fully demonstrated that it possessed peculiar properties. The minerals called *spodumene* and *lepidolite* also afford the same substance, to which the term *lithia*, deduced from its lapideous original, has been applied. It has also been detected in several varieties of mica, and by Berzelius in the waters of Carlsbad in Bohemia.

Method of obtaining lithia.

1062. The best process for preparing lithia is that of Berzelius. One part of petalite or spodumene, in fine powder, is intimately mixed with two parts of fluor spar, and the mixture is heated with three or four times its weight of sulphuric acid, as long as any acid vapours are disengaged. The silica of the mineral unites with fluoric acid, and is dissipated in the form of fluosilicic acid gas, while the alumina and lithia unite with sulphuric acid. After dissolving these salts in water, the solution is boiled with pure ammonia to precipitate the alumina, filtered, evaporated to dryness and then heated to redness to expel the sulphate of ammonia. The residue is sulphate of lithia.* T. 353.

Action of galvanism.

1063. When lithia is submitted to the action of the Voltaic pile, it is decomposed with the same phenomena as potassa and soda; a brilliant white and highly combustible metallic sub-

* For other methods see Henry's *Chemistry*, I. 572.

stance is separated, which may be called *lithium*, the term *lithia* being applied to its protoxide.

The properties of this metal have not hitherto been investigated, in consequence of the difficulty of procuring any quantity of its oxide.

1064. The proportion, in which this metal unites with oxygen, has, of course, not been determined by direct experiment; but it has been deduced by Vauquelin, from an analysis of the sulphate of lithia, and the application of the law that the proportion between the oxygen of sulphuric acid and that of the bases which it saturates is as 3 to 1, to be as follows:

| | | | | | | |
|---------|-----|-------|-------|-----|-------|-------|
| Lithium | . . | 56,50 | . . . | 100 | . . . | 130 |
| Oxygen | . . | 43,50 | . . . | 77 | . . . | 100 |
| | | | | | | <hr/> |
| | | | | | | 100, |

Arfwedson's estimate scarcely differs from this, but Gmelin deduces the composition of lithia to be 58,05 metal + 41.95 oxygen. On the whole we may consider the atomic weight of lithium to be represented by 10, and lithia by that number + 8 = 18. H. 1. 574.

1065. Pure lithia is very soluble in water, and its solution tastes acrid like the other fixed alkalis. It acts powerfully on vegetable blues, converting them to green. It is very sparingly soluble in alcohol.

1066. *Chloride of Lithium*, obtained by evaporating the muriate to dryness, and fusing it, is a white semitransparent substance. It evidently differs from the chlorides of potassium and sodium, in being extremely deliquescent; in being soluble in alcohol; in being decomposed when strongly heated in the open air, when it loses chlorine, absorbs oxygen, and becomes highly alkaline; in being very difficultly crystallizable; and in tinging the flame of alcohol of a red colour.*

1067. *Muriate of Lithia* forms small regular cubes very similar to common salt in their taste. The easiest mode of obtaining the crystals is to expose the solution to the sun in a hot day. The crystals deliquesce very speedily when exposed to the air, but not with so much rapidity as nitrate of lithia. This salt does not melt when exposed to the red heat produced by the action of a spirit lamp; but when exposed in a platinum crucible, not completely covered, to an incipient white heat, it is fused into the chloride. U. 565.

1068. *Nitrate of Lithia* is very soluble, and by evaporation crystallizes in regular rhomboids, sometimes in needles. It is extremely fusible and on cooling attracts moisture and becomes fluid.

1069. *Sulphuret of Lithium*.—With sulphur lithia affords a very soluble yellow compound which is decomposed by acids, with the same phenomena as the alkaline sulphurets, and, from

* *Nitrate of Lithia* is a very soluble deliquescent salt, fusible and decomposed by heat; its taste is cooling; it crystallizes in rhomboids.

the abundance of the precipitate appears to contain a large proportion of sulphur.

Sulphate.

1070. *Sulphate of Lithia* crystallizes in small prisms, perfectly white, and possessed of much lustre. Their taste is saline, and their solubility intermediate between that of sulphate of potassa and sulphate of soda. The crystals contain no water, and fuse at a heat below redness. Their solution occasions no change in solution of platinum, nor in tartaric acid: They consist of

Composition.

| | | | |
|----------------------|------|----|-------------|
| Sulphuric acid . . . | 54,7 | or | 1 atom = 40 |
| Lithia | 20,9 | or | 1 " = 18 |
| Water | 13,4 | or | 1 " = 9 |

100, atomic weight 67

Phosphate.

1071. *Phosphate of Lithia* may be obtained by adding phosphoric acid to sulphate of lithia; no precipitate is at first formed, but on adding excess of ammonia, an insoluble phosphate of lithia falls. This property enables us to separate lithia from potassa and soda. The phosphate of lithia may be decomposed by dissolving it in acetic acid and adding acetate of lead: *acetate of lithia* remains in solution.

Carbonate.

1072. *Carbonate of Lithia*.—When a strong solution of carbonate of potassa is added to sulphate of lithia, a white precipitate of *carbonate of lithia* is formed. It requires about 100 parts of water at 60° for its solution. It is fusible, alkaline, effervesces with acids, and absorbs carbonic acid from the air. Lithia and its carbonate, when heated upon platinum, act upon that metal.*

Composition.

It consists of 1 lithia + 1 acid. The watery solution effervesces with acids; changes vegetable blue colours to green; decomposes solutions of alumina and magnesia, and of the metals; is rendered caustic by lime; disengages ammonia from its combinations; and does not precipitate the muriate of platinum.

Distinctive characters.

1073. Lithia, then, is sufficiently distinguishable both from potassa and soda, by the difficult solubility of its carbonate in water; by affording deliquescent salts with muriatic and nitric acids; and still more by its higher capacity of saturation. It agrees with soda in not being precipitated by tartaric acid or muriate of platinum, but the salts of lithia, when their concentrated solutions are mixed with one of carbonate of soda, deposite carbonate of lithia. H. 1. 575. All the salts of lithia, when heated on platinum wire before the blow-pipe tinge the flame of a red colour.†

* The platinum crucible in which carbonate of lithia has been exposed to a red heat, gives obvious indications of having been attacked, its surface assuming a dark olive-green colour; but the metallic lustre is rest. red by rubbing the crucible with coarse sand and water.

† For an analysis of Lithion micas and the distinguishing properties of lithia, see Dr Turner's papers, *Edin. Jour.* iii. 137, 261, &c.

The following is M. Berzelius's method of discovering lithia in any solution. Precipitate the lime by oxalate of potassa, separate the magnesia by carbonate of soda, but the mixture must be evaporated to dryness, and the residue fused; for otherwise some of the magnesia would be easily redissolved in

SECTION V. *Calcium.*

1074. When lime is electrized negatively in contact with mercury, an amalgam is obtained, which, by distillation, affords a white metal. It has been called *calcium*, and when exposed to air, and gently heated, it burns and produces the *oxide of calcium*, or *lime*.*

How obtained.

To obtain calcium, a paste may be moulded, either of pure lime, or of sulphate of lime and water, into the shape of a small capsule, which may be placed on a metallic dish. Into this capsule mercury may be poured, and connected with the negative extremity of a galvanic apparatus of sufficient power, while the positive wire of the same pile is made to touch the under surface of the metallic plate. When the contact has been continued sufficiently long, an amalgam of mercury and calcium is obtained, which may be put into a small retort, along with naphtha enough to cover it. The retort is then to be connected with a tubulated receiver, the tubulure of which is only loosely stopped with a cork. On applying heat, the naphtha first comes over; then the mercury; and the calcium remains, surrounded by an atmosphere of vapour of naphtha. As the vessels cool, it would be desirable, and would not be difficult, to fill them with nitrogen gas, to prevent the oxidation of the calcium. H. 1. 575.

Lime appears to consist of 20 parts of this metallic base united to 8 parts of oxygen, so that its representative number will be = 28.

1075. The combinations of lime are very abundant natural products, and of these the *native carbonate* which, more or less pure, constitutes the different kinds of marble, chalk, and limestone, and which is also the hardening principle of shell, coral, &c., may be considered as the most important.

Native carbonates of lime.

Lime may be obtained in a state of considerable purity by exposing powdered white marble to a white heat, which expels the carbonic acid. To obtain absolutely pure lime, white marble may be dissolved in dilute muriatic acid, a little ammonia added to the solution, and filtered: carbonate of ammonia is then added, and the precipitate dried, washed, and exposed to a white heat.

Method of obtaining lime.

1076. Its colour is light grey; it is acrid and caustic and converts vegetable blues to green; its specific gravity is 2,3; it is

Properties.

the form of a double carbonate of soda and magnesia. The mass, taken up by the water and filtered, will not give any further precipitate even when pure phosphate of soda is added; but if it contains lithia, it will become turbid during the evaporation, which must be continued till the matter be perfectly dry. It is next redissolved in a very small quantity of cold water, which leaves undissolved a double phosphate of soda and lithia, equivalent to $\frac{1}{3}$ of its weight of carbonate of lithia. The characters which distinguish this phosphate from the earthy phosphates with which it may be confounded, are as follows. It is very fusible before the blow-pipe. When melted with carbonate of soda, it enters with the soda into the charcoal. On a leaf of platinum the melted mixture is limpid. The earthy phosphates remain on the charcoal while the soda penetrates it, and do not give a limpid mixture when they are melted on a leaf of platinum. With twice its weight of carbonate of lime it fuses at a red heat, without, however, attacking the platinum, as lithia ordinarily does: but if some drops of water are added to it, and afterwards evaporated, the platinum becomes yellow all round when the mass is heated anew.—*Edin. Philos. Jour.* iv. 128.

* Or *Quick-lime* as it is popularly termed from its corrosive properties.

very difficult of fusion, but remarkably promotes the fusion of most other earthy bodies, and is therefore used in several metallurgic processes as a cheap and powerful flux. When quite pure it can only be fused in very minute particles by the oxygen blow-pipe, or by the Voltaic flame.* It is an essential ingredient in mortar, and other cements used in building. Exposed to air it becomes white by the absorption of water and a little carbonic acid.

Hydrate:

1077. When a small quantity of water is poured upon lime, there is a great rise of temperature resulting from the solidification of a portion of the water, and a white powder is obtained, called *slaked lime*, which is a *hydrate*, and which appears to consist of one proportional of water = 9 + one proportional of lime = 28 = 37 hydrate.

It is strictly a *proto-hydrate*. Some care is necessary in its preparation, lest more water should be added, than is essential to its constitution. It affords a very convenient form of keeping lime, for occasional use in a laboratory; for the hydrate may safely be preserved in glass bottles, which are almost constantly broken by the earth, if enclosed in its perfectly dry state.

Phenomena attending the slaking of lime.

1078. The degree of heat produced by the combination of lime with water, is supposed by Mr Dalton to be not less than 800°, and is sufficient to set fire to some inflammable bodies: and when a large quantity of lime is suddenly slaked in a dark place, even light, according to Pelletier, is sometimes evolved. The caloric, which is thus set at liberty, is doubtless that contained in the water, and essential to its fluidity. By combination with lime, water passes to a solid state, and probably even to a state of much greater solidity than that of ice;† Hence, during this change, it evolves more caloric than during conversion into ice; and hence even ice itself, when mixed with quicklime, in the proportion of one to two, enters into a combination which has its temperature raised to 212°. When a sufficient quantity of water has been added to reduce lime into a thin liquid, this is called *milk* or *cream of lime*; but this can scarcely be regarded as a definite compound.

1079. Lime, though not of itself volatile, is, in some manner, perhaps mechanically, carried up by the vapour employed in slaking it. When a piece of moistened paper, stained with the juice of the violet, is held in the steam, which arises from lime suddenly slaked, its colour is changed from blue to green. Hence the smell which is perceived during the slaking of lime. H. 1. 577.

Crystallized.

1080. Lime may be obtained in a crystalline form by placing lime-water under the receiver of an air-pump, with another

* The utmost light is given by lime exposed on burning charcoal to the heat excited by a jet of oxygen gas falling upon it. See Liéut. Drummond's expts. *Edin. Jour. of Science*.

† According to M. Bellani, there is no ultimate condensation between the elements of the hydrate. *Quart. Jour. N. S. v. 225*.

vessel of sulphuric acid. The water is thus slowly evaporated, and imperfect crystals of hydrate of lime are formed.*

Lime is very sparingly soluble in water, viz. in the proportion of about 1 to 700.†

1081. Lime-water is limpid and colourless; its taste is nauseous, acrid, and alkaline, and it converts vegetable blues to green. Lime water. It is usually prepared by pouring warm water upon powdered lime, and allowing the mixture to cool in a close vessel: the clear part is then decanted from the remaining undissolved portion of lime. When lime-water is exposed to the air, a pellicle of carbonate of lime forms upon its surface, which if broken, is succeeded by others, until the whole of the lime is thus separated in the form of an insoluble carbonate. Lime-water is used in medicine as an antacid.

1082. When oxygen is passed over heated lime, it is absorbed, and a portion of *peroxide of calcium* is formed. A hydrated peroxide of calcium is thrown down, according to M. Thenard, when lime-water is dropped into oxygenated water.

1083. *Chloride of Calcium* is produced by heating lime in chlorine, in which case oxygen is evolved; or by evaporating *muriate of lime*, obtained by dissolving carbonate of lime in muriatic acid, to dryness, and exposing the dry mass to a red heat in close vessels. In this case the muriatic acid is decomposed; its hydrogen, uniting with the oxygen of the lime, escapes in the state of water; and the chlorine unites with the calcium. The chloride and the muriate are, therefore, mutually convertible by adding or expelling water. Chloride of calcium.

1084. It consists of 20 calcium + 36 chlorine = 56. This compound has a strong attraction for water; it deliquesces when exposed to air, and becomes what used to be called *oil of lime*. It is difficultly crystallizable from its aqueous solutions; with care, however, it may be obtained in six-sided prisms, consisting of the chloride combined with water. It is most readily crystallized by exposing its solution to the temperature of 32° . Its taste is bitter and acrid; one part of water at 60° dissolves four parts of the chloride. Its solubility, however, is greatly influenced by temperature, for at 32° one part of water will not dissolve more than two of the salt, and at 212° it takes up nearly any quantity. It is copiously soluble in alcohol, and much heat is evolved during the solution. When fused it acquires a phosphorescent property, as was first observed by Homberg, and hence termed *Homberg's phosphorus*. It is abundantly produced in the manufacture of carbonate of ammonia, from the decomposition of muriate of ammonia by lime, and hence has Composition and Properties.

Homberg's phosphorus.

* Gay-Lussac, *Annales de Chimie et Phys.* i. 334.

† According to Thomson 1 to 758. The experiments of Mr Dalton tend to establish a curious fact respecting the solubility of lime, viz. that it dissolves more plentifully in cold than in hot water, he found that at 60° F. 778 grains of water dissolve 1 grain of lime and at 212° , 1270 grains were required. He further infers that at the freezing point water would probably take up nearly twice as much lime as is dissolved by boiling water—this has been confirmed by Mr R. Phillips.—*Ann. Philos. N. S.* 1. 107.

Uses.

sometimes been called *fixed sal ammoniac*. The production of cold by mixing muriate of lime with snow has already been adverted to (147.) Chloride of calcium absorbs ammoniacal gas in considerable quantities.* In its fused state this compound is very useful for drying certain gaseous bodies, but where the quantity of the gas is to be ascertained, its powers of absorption in certain cases must not be overlooked.

Bleaching powder.

Peletier has stated, that if carbonic acid be passed through a solution of muriate of lime, the whole becomes a hard solid mass. If sulphuric acid be poured into a strong solution of muriate of lime, the whole congeals into a solid mass of sulphate of lime.

1085. A substance called *Oxymuriate of Lime or bleaching powder* is abundantly employed as a bleaching material, and manufactured by passing chlorine into leaden chambers containing hydrate of lime in fine powder, by which the gas is copiously absorbed. It is a dry white powder, which smells faintly of chlorine, and has a strong taste. It dissolves partially in water, and the solution possesses powerful bleaching properties, and contains both chlorine and lime; while the undissolved portion is hydrate of lime retaining a small quantity of chlorine.

1086. The aqueous solution is decomposed by exposure to the air, chlorine being set free, and carbonate of lime generated.

1087. The composition of this salt has been investigated by Dalton,† Thomson,‡ Welter§ and Ure.|| The three first named chemists infer that the bleaching powder is a hydrated *sub-chloride* or *di-chloride* in which 36 parts or 1 atom of chlorine are united with 56 parts or 2 atoms of lime. Dr Ure maintains that the elements of the compound do not constitute a regular atomic combination.* **

Fluate.

1088. *Fluoride of Calcium—Fluor Spar.*—Fluor spar is a mineral found in many parts of the world, but in great beauty

* Faraday, *Journal of Science*, vol. v. p. 74.

† *Ann. Philos.* vol. i. and ii.

‡ *Ibid.* vol. xv.

§ *Ann. de Chim. et de Phys.* viii.

|| *Quart. Jour.* xiii.

¶ The assay of sub-chloride of lime, in order to ascertain its commercial value, has been effected in several ways.

For the purposes of the artist, the most practicable method will be found to be the test of solution of indigo in sulphuric acid. It may be of such strength that 1600 parts of the liquor contain one of indigo. Of this solution 100 cubic inches of chlorine = $76\frac{1}{2}$ grains, destroy the colour of 1159.5 cubic inches, or 10 grains of chlorine discharge the colour of 152 cubic inches of the solution. It is desirable to dilute the solution of chloride, so that its volume may be nearly one-half that of the colour test; to pour the former into the latter slowly and at intervals, stirring the mixture well after each addition; and in making several comparative experiments to take care that the quality of the test, and the manner of proceeding, shall be the same in all. It cannot, however, be pretended that this test possesses the scientific accuracy attainable by the admeasurement of the disengaged chlorine, which alone is to be depended upon, when a precise analysis is required. H. 1. 584.—M. Gay-Lussac has contrived an apparatus which he calls a *chlorometer*, for the assay of this substance. See *Ann. Philos.* viii. 218.

Chlorate.

** *Chlorate of Lime* is a very soluble deliquescent salt of a sharp bitterish taste. It is most easily produced by dissolving carbonate of lime in chloric acid. Exposed to heat, oxygen is evolved, and a chloride formed.

Iodate of Lime is difficultly crystallizable in small quadrangular prisms. *Hydriodate of Lime* is very deliquescent; when dried it becomes *iodide of calcium*, a white fusible compound.

and abundance in England, and especially in Derbyshire. Here it is commonly called *Derbyshire spar*, or by the miners of that country *blue John*. It is usually found in cubic crystals, which may easily be cleaved into octoëdra, sometimes considered as its primitive form. Its colours are extremely various. Its specific gravity is 3.15. It is perfectly tasteless and insoluble in water. When thrown in powder upon a plate of iron heated below redness in a dark place, it emits a phosphorescent light.

Compact fluor is a scarce variety: the finest specimens come from the Hartz. A third variety is *chlorophane*, so called from the beautiful pale green light which it exhibits when heated. Compact.

The nature of the colouring matter of fluor spar is not exactly understood. It is liable to fade, and the blue varieties become red and brown by heat.

1089. When a mixture of one part of the purest fluor spar in fine powder is distilled with two of sulphuric acid; sulphate of lime remains in the retort, and a highly acrid and corrosive liquid passes over, which requires the assistance of ice for its condensation which is *Hydro-fluoric acid*. Hydro-fluoric acid.

Fig. 122 represents an apparatus for the formation of this acid. *a* an alembic with a head, from which passes the tube *b* made to fit the neck of the bottle *c*; *d* is a cover which may be substituted for the head when the alembic is used for other purposes, *e* a stopple ground to fit the neck of the bottle *c*. All the parts of this apparatus should be made of pure silver, for glass is instantly acted upon. The alembic may be of the capacity of 16 fluid ounces, that of the head and tube $2\frac{1}{2}$ and that of the receiver $3\frac{1}{2}$ ounces. With an apparatus of this size, about two ounces of pure fluor spar and four ounces of sulphuric acid may be employed. These materials being introduced into the alembic, and the head fitted on, it should be placed under a flue, the bottle or receiver being surrounded with ice and rather loosely connected with the tube. The heat required is not considerable; a few live coals being applied beneath the alembic, the acid will be condensed, and will condense in the bottle.* Method of obtaining.
Pl. vii.

1090. This acid is colourless, of a very pungent smell and extremely destructive. If applied to the skin it instantly kills the part, producing extreme pain, and extensive ulceration. The fumes instantly and powerfully corrode glass, and the contact of them with the skin, or lungs, should be carefully avoided. At 80° this acid becomes gaseous; it has never been frozen; it produces white fumes when exposed to a moist air, and occasions a hissing noise when dropped into water. Properties.

1091. This acid acts upon potassium and sodium, and some other metals with great energy; hydrogen is evolved, and a peculiar compound, probably the basis of the acid, and the metal results.

Its composition is probably 1 atom of fluorine + 1 of hydrogen.† (368). Composition,

1092. Fluoric acid, it is remarked by Berzelius, is distinguished by its great capacity of saturation; for 100 parts combine how distinguished.

* Silliman, *Amer. Jour. of Science*, vi. 355.

† The discovery of M. Kuhlmann that fluor spar cannot be decomposed by anhydrous sulphuric acid is an additional fact in favour of the opinion that fluor spar is a fluoride of calcium.—*Ann. de Chim. et de Phys.* Feb. 1827.

with a quantity of base containing 74,72 parts of oxygen, and the compound is then neutral. Many of its salts are readily soluble; but they cannot be obtained quite neutral in a solid form, being found in that state to have an excess of one or other ingredient. Its compounds with alkalis crystallize with an excess of acid and attack glass. Fluoric acid is also distinguished by the property of forming, with acids weaker than itself, compounds in which the latter serve as a kind of base. Berzelius finds that it is susceptible of forming combinations, not only with silica and with boracic acid, but with titanio, columbic, tungstic and molybdic acids; and that these compound acids, dissolved in water, are analogous to liquid fluo-silicic acid, and that the water may be replaced by other bases, forming distinct genera of salts, called fluo-titanites, fluo-tungstates, &c.* H. 1. 282.

Uses.

1093. Hydro-fluoric acid has been used for the purpose of etching on glass,† but requires to be diluted with three or four parts of water. The glass should be covered with a varnish, prepared by melting together bees-wax and turpentine, and surrounded at the edge by a rim of the same. The varnish is then to be removed wherever it is desired to have the acid act upon the glass, as in the process for etching on copper.‡

Neutral fluates.

1094. The neutral fluates of fixed bases are fusible at a high temperature, and most of those which have been examined may be heated in close vessels to any intensity, if quite dry, without decomposition. The fluates of the alkalis and alkaline earths are not decomposed, so far as is known, by heat and combustible matter; nor does any acid, except the boracic, effect their decomposition, provided they are free from moisture. When digested, on the contrary, in concentrated sulphuric, phosphoric, or arsenic acids, the fluoric acid is disengaged. T. 491.

Nitrate.

1095. *Nitrate of Lime* is a deliquescent salt, soluble in 4 parts of water at 60°. It is found in old plaster and mortar, from the washings of which, nitre is procured by the addition of carbonate of potassa.

Preparation of

1096. To prepare it artificially, nitric acid, diluted with five or six parts of water, may be saturated with carbonate of lime, 63 parts of which are decomposed by 90,23 of nitric acid of density 1,5, and give 103,05 of dry nitrate of lime.§ When this solution is boiled down to the consistence of syrup, and exposed in a cool place, long prismatic crystals are formed, resembling, in their disposition, bundles of needles diverging from a common centre. These crystals are readily soluble in

* See *Ann. de Chim. et de Phys.* xxix.

† For more minute directions, see Faraday's *Chem. Manip.* sect. xxiii. 1251.

‡ M. Varinsky has given the name of *Iodo-fluoric acid* to crystals of a fine golden yellow colour, and possessing all the properties of a strong acid, which he obtained on mixing the vapours of iodine and fluoric acid. They dissolve more readily in hot than in cold water, and with potassa produce a gelatinous salt, having a very disagreeable bitter taste.—*Quart. Jour.* N. S. v. 224.

§ Phillips' *Journal of Science*, v. 167.

water, of which, at 60°, they require two parts, and boiling water dissolves an equal weight. They deliquiate speedily, when exposed to the air; and are decomposed at the temperature of ignition. Exclusive of water it contains,

| | Acid. | Base. | |
|-----------------------------|-------|-------|------------|
| According to Dalton | 61,3 | 38,7 | |
| Phillips | 65,6 | 34,4 | H. 1. 586. |

1097. When a solution of nitrate of lime is evaporated to dryness in an earthen vessel, then fused for five or ten minutes in a crucible, and poured while in fusion into an iron pot previously heated, the congealed mass forms *Baldwin's phosphorus*. It must be broken into pieces, and preserved in a well-stopped phial. These pieces, after having been exposed to the sun for a few hours, emit in the dark a beautiful white light, affording one variety of solar phosphorus. At a red heat it is decomposed; its acid is dissipated, and pure lime remains. It contains in its crystallized state about 25 per cent. of water, and may hence be considered as composed of

| | |
|--------------------------------------|----|
| 1 proportional dry nitrate | 82 |
| 3 ————— water | 27 |

109 B.

1098. *Sulphuret of calcium* was formed by Berzelius by passing hydrogen gas over red-hot lime, the oxygen of which united with the hydrogen, to form water, while the sulphur united with the calcium. Berthier formed it, also, by exposing anhydrous sulphate of lime to a strong heat in a charcoal crucible. In both cases a sulphuret of calcium was formed completely soluble in water, and constituted of

| | | | |
|-----------------|-------|----------------|------------|
| Calcium | 59,09 | or 1 atom = 28 | |
| Sulphur | 40,91 | " 1 " = 16. | H. 1. 581. |

1099. *Hydro-sulphuret of lime* is obtained by transmitting a current of sulphuretted hydrogen gas through water in which lime is kept mechanically suspended. It is crystallizable, and the crystals are colourless and readily soluble in water.

1100. *Hydroguretted sulphuret of lime* is formed whenever the sulphuret of calcium is dissolved in water, or by boiling together three parts of hydrate of lime, one of sulphur, and ten of water. The compound has a deep orange colour, and derives importance from its use as an eudiometrical test. From the experiments of Vauquelin it seems probable that it is subject to a variety in its proportions, and to corresponding differences in its properties.* H. 1. 591.

1101. According to Mr Herschel, crystallized *hydrosulphuret* of lime is formed when three parts of slaked lime and one of sulphur are boiled in twenty parts of water, and the solution allowed to cool upon the sediment: he dried the crystals by exposure to the absorbent power of a large surface of sulphuric acid, placed under an exhausted receiver. Their form is that

* *Ann. de Chim. et de Phys.* vi. 39.

of quadrilateral prisms with dihedral summits. They are sparingly soluble in cold water, the solution having a yellow colour and an acid, bitter, and sulphurous taste. They consist of two proportionals of lime, two of sulphur, one of hydrogen, and four of water.*

1102. When sulphurous acid is ground in a mortar with the above crystals its smell disappears, and when filtered it is found to be a solution of *hyposulphite of lime*. By passing sulphurous acid through an aqueous solution of sulphuret of lime, the same product is obtained: and if the solution be filtered and evaporated, at a temperature not exceeding 140° , it furnishes crystals: the temperature of ebullition decomposes it. The crystals are little altered by air, very soluble in water, and insoluble in alcohol. They consist, according to Mr Herschel, of

| | |
|-----------------|-------|
| Lime | 21,71 |
| Acid | 36,71 |
| Water | 41,58 |

100†

1103. *Sulphite of Lime* is formed by passing sulphurous acid into a mixture of lime and warm water. It is a white powder, soluble by excess of sulphurous acid, and then separating in prismatic crystals, of difficult solubility, efflorescent, and passing into sulphate of lime by exposure to air.

1104. *Sulphate of Lime* occurs native in selenite, gypsum, and plaster-stone. Sulphate of lime may be formed, by adding to the carbonate a sufficient quantity of sulphuric acid; and by gently calcining the residue, to expel the redundancy of the latter acid; it then affords silky crystals soluble in 350 parts of water. When these, or the native crystallized sulphate are exposed to a red heat, they lose water, and fall into a white powder (*plaster of Paris*), which, made into a paste with water, soon solidifies. Dry sulphate of lime consists of 28 lime + 40 sulphuric acid = 68. Crystalline sulphate of lime contains two proportionals of water, and is consequently represented by $68 + 18 = 86$.

1105. As sulphate of lime is more soluble in water than pure lime, sulphuric acid affords no precipitate when added to lime-water. Nearly all spring and river water contains this salt, and in those waters which are called *hard* it is abundant. They curdle soap, the alkali of which is detached by the sulphuric acid, and the oil is set at liberty. It gives to them a slightly nauseous taste. At a very high temperature sulphate of lime is fusible, but it suffers no decomposition; heated with charcoal it is converted into a sulphuret. It dissolves without decomposition in dilute nitric and muriatic acids, and separates from these solutions

* *Edinburgh Philosophical Journal*, i. p. 11. &c.

† The hyposulphites of soda, potassa, and ammonia, of baryta, and of strontia, may be formed by passing sulphurous acid through the aqueous solutions of their sulphurets.

when concentrated, in long, silky or transparent crystals. It is decomposed by the alkaline carbonates, a double exchange of principles ensuing. Hence the milkiness which ensues on adding carbonate of potassa to many spring waters; the carbonate of lime, which is generated, being less soluble than the sulphate.

1106. *Native Sulphate of Lime* occurs in various forms. Native. The crystallized variety is usually called *selenite*; the fibrous and earthy, *gypsum*; and the granular or massive, *alabaster*. The primitive form of selenite is a *right oblique-angled prism*.*

The crystals are commonly transparent, and of various colours; it is softer than native carbonate of lime, and yields very easily to the nail. It is seldom found in veins, but generally disseminated in argillaceous strata. It is often accompanied by shells and pyrites, and appears to have resulted from their mutual decomposition. A beautiful fibrous variety is found in Derbyshire, applicable to ornamental purposes. It is turned by the lathe, and sculptured into a variety of beautiful forms, more especially by the Florentine artists. Anhydrous.

1107. There is a variety of sulphate of lime, which has been called *anhydrous gypsum*, or *anhydrite*, in reference to its containing no water. It is harder than selenite, and sometimes contains common salt, and is then called *muricite*. It is rarely crystallized, generally massive and lamellar, and susceptible of division into rectangular prisms. It has a pale blue tint; sometimes it is pink or reddish and often white. It has been found at Vulpino, in Italy, and hence called *Vulpinite*. The statuaries of Bergamo and Milan employ it, and artists know it by the name of *Marbre di Bergamo*. A compound of sulphate of lime and sulphate of soda is found in the salt-mines of New Castile, which mineralogists have described under the name of *Glauberite*.

1108. *Phosphuret of Lime*.—By passing phosphorus over red-hot lime, a brown compound is produced, which rapidly decomposes water with the evolution of phosphuretted hydrogen gas. Phosphuret. *Hydrophosphuret* and *hydro-phosphite of lime* are also formed. This compound, though called phosphuret of lime, is probably a *phosphuret of calcium*.

The best process for obtaining it is the following :

Select a green glass, or porcelain tube, closed at one end, and about 18 inches long, and one inch diameter, and carefully cover it with a clay lute containing a very little borax. Put an ounce of phosphorus broken into small pieces into the lower end, and fill it up with pieces of clean quicklime, about the size of large peas : place it in an inclined position in a furnace, so that the end containing the phosphorus may protrude, while the upper part of the tube is heating to redness; then slowly draw the cool part into the fire, by which the phosphorus will be volatilized, and passing into the red-hot lime, convert a portion of it into phosphuret. Care should be taken that no considerable portion of phosphorus escapes and burns away at the open end of the tube, How prepared.

Properties.

* Brooke's *Crystallography*.

which after the process, should be corked and suffered to cool. Its contents may then be shaken upon a sheet of paper, and the brown pieces picked out and carefully preserved in a well stopped phial; the white pieces, or those which are only pale brown, must be rejected.

1109. The phosphuret of calcium has the remarkable property of decomposing water at the common temperature of the atmosphere; and the water afterwards contains phosphite, or hypo-phosphite, not phosphate of lime.*

Exp. Drop a small piece of it into a wine-glass of water, and in a short time bubbles of phosphuretted hydrogen gas will be produced; which, rising to the surface will take fire, and explode. If the phosphuret of lime be not perfectly fresh, it may be proper to warm the water to which it is added.†

Exp. Into an ale-glass put one part of the phosphuret in pieces of about the size of a pea (not in powder), and add to it half a part of chlorate of potassa. Fill the glass with water, and put into it a funnel, with a long pipe, or narrow glass tube, reaching to the bottom. Through this pour three or four parts of strong sulphuric acid, which will decompose the chlorate; and, the phosphuret also decomposing the water at the same time, flashes of fire dart from the surface of the fluid, and the bottom of the vessel is illuminated by a beautiful green light.‡

Phosphate. 1110. *Phosphate of Lime* exists abundantly in the bones of animals; it is also found in minerals. It may be obtained by dissolving bones, which have been well calcined and then pulverized, in dilute muriatic acid, and precipitating the solution with pure ammonia. The precipitate, when sufficientlyedulcorated, is *phosphate of lime*. It may be formed artificially, by mixing solutions of phosphate of soda and muriate of lime. It is insipid and insoluble in water, but dissolves in dilute nitric and muriatic acid without decomposition, and is precipitated unaltered by caustic ammonia. It is decomposed by sulphuric acid, and thus the phosphoric acid for the production of phosphorus is usually procured (643.) It consists of 28 lime + 28 phosphoric acid = 56.

At a very high temperature phosphate of lime fuses into an opaque white enamel.

Bi-phosphate. 1111. *Bi-phosphate of Lime* is formed by digesting the phosphate in phosphoric acid. On evaporation a white deliquescent uncrystallizable mass is obtained, composed of one proportional of lime + two of phosphoric acid.

Tri-phosphate. 1112. *Tri-phosphate of lime*, according to Mr Dalton may be formed by adding pure phosphoric acid to lime water, till a commencement of precipitation appears, when the solution must be cleared by a drop or two of acid. If the solution be evaporated to dryness at a moderate heat, and then dissolved in water again, simple phosphate of lime remains, and a quadri-phosphate exists in the solution.

Quadri-phosphate. 1113. *Quadri-phosphate of Lime*.—If 100 parts of phosphate of lime be digested for 24 hours with 87 parts of sulphuric acid, diluted with a sufficient quantity of water, and be

* Gay-Lussac, 85 *Ann. de Chim.* 206, and *Ann. de Chim. et Phys.* vi. 328.

† Dr Book first suggested that the production of the phosphuretted hydrogen is the result of the action of phosphuret of calcium and not of lime. See *Amer. Jour.* xii. 294.

‡ Davy.

then filtered, the liquid which passes through contains the whole of the phosphoric acid, with only one-fourth of the lime which existed in the original salt, the remaining $\frac{3}{4}$ ths having formed an insoluble compound with the sulphuric acid. The dissolved salt is therefore a compound of 1 atom of lime = 28 + 4 atoms of acid = 112. When evaporated it forms, on cooling, pearly scales, which have an acid taste, and dissolve readily in water, giving a solution of the sp. gr. 1,44. When dried and fused in a crucible, a transparent glass is obtained, commonly called *glacial phosphoric acid** (656). H. 1. 591.

1114. *Carbonate of Lime*.—Lime has a strong attraction for *carbonic acid*, but not when perfectly dry; for if a piece of dry quicklime be passed into a jar of carbonic acid gas over mercury, no absorption whatever ensues. But if a bottle, filled with carbonic acid gas, be inverted over a mixture of lime and water of the consistence of cream, a rapid absorption will be observed, especially if the bottle be agitated; or if a jar or bottle, filled with carbonic acid, be brought over a vessel of lime water on agitating the vessel, a rapid diminution will ensue, and the lime water will become milky.

Carbonate.

When a shallow vessel of lime water is exposed to the air, a white crust forms on the surface, and this, if broken, falls to the bottom, and is succeeded by another till the whole of the lime is precipitated from the solution. This is owing to the absorption of carbonic acid gas from the air by the lime, which is thus rendered insoluble in water. Dry lime, also, when exposed to the atmosphere, first acquires moisture, and, having become a hydrate, next absorbs carbonic acid. In a sufficient space of time, all the characters distinguishing it as lime disappear, and it acquires the property of effervescing with acids. The strong affinity of lime for carbonic acid enables it to take this acid from other substances. Thus carbonates of alkalies are decomposed by lime (961). H. 1. 587.

1115. Carbonate of lime occurs in nature in great abundance and in various forms. The primitive form of crystallized carbonate of lime, or *calcareous spar*, is an obtuse rhomboid of $105^{\circ} 5'$ and $74^{\circ} 55'$. Its specific gravity is 2,7. It occurs in every kind of rock, and its secondary forms are more numerous than those of any other substance: sometimes it is deposited from its solution in water acidulated by carbonic acid, and substances immersed in this water become incrustated by carbonate of lime.

Calcareous
spar.

1116. The carbonic acid existing in carbonate of lime is expelled by a strong red heat. If distilled in an earthen retort, carbonic acid gas is obtained, and lime remains in the retort in a pure or caustic state. By this process carbonate of lime loses about 45 per cent.

Carbonic
acid expelled
by heat.

* *Native phosphate of Lime* has by some been regarded as a *sub-phosphate*, in which case it would be composed of two proportionals of lime + one phosphoric acid. This compound occurs crystallized and massive, and is known under the names of *apatite*, *asparagus-stone*, and *phosphorite*. Native.

Sir James
Hall's expe-
riments.

1117. The experiments of Sir James Hall have proved, that when the escape of the carbonic acid is prevented by strong pressure, carbonate of lime is fusible in a heat of about 22° of Wedgwood's pyrometer.* And Mr Bucholz has lately fused this substance, by the sudden application of a violent heat, without additional compression.†

Decomposed
by acids.

1118. Carbonate of lime is precipitated by the carbonated alkalies from solutions of muriate, nitrate, and sulphate of lime. It is decomposed by almost all acids. This will appear if upon chalk or marble contained in a gas bottle diluted sulphuric or muriatic acid be poured. A violent effervescence will ensue, owing to the escape of carbonic acid gas, which may be collected over water or mercury. By a little modification of the experiment, the quantity of carbonic acid expelled from the carbonate may be correctly ascertained. Let 100 grains of carbonate be put into a Florence flask, with an ounce or two of water; place this in the scale of a balance; and in the same scale, but in a separate bottle, about half an ounce of muriatic acid. Add the muriatic acid to the carbonate as long as any effervescence is produced, and then blow out that part of the disengaged carbonic acid which remains in the flask, by a pair of bellows. Ascertain, by adding weights to the opposite scale, how much has been lost; suppose it to be 43,5 grains; this shows the quantity of carbonic acid disengaged. Calcine another 100 grains in a covered crucible. It will lose rather more of its weight; because, besides its carbonic acid, all the water is expelled which it may contain. Let this loss be stated at 45 grains; the former loss deducted from this (45—43,5) or 1,5 grains, shows the quantity of water in 100 of the carbonate. The proportion, however, thus discovered, is so small that it may be considered as an accidental ingredient. Independently of water it is constituted,

| | Acid. | Base. |
|-------------------------------|-------|-------|
| According to Dr Wollaston, of | 43,7 | 56,3 |
| ———— Berzelius, of | 43,6 | 51,4 |

Its true composition is probably one atom of acid + 1 of base.

Borate.

1119. *Borate of Lime* may be formed by adding a solution of boracic acid to lime water. The resulting compound is a white tasteless powder, which dissolves very sparingly in water.

Seleniate.

1120. *Seleniate of Lime*.—Selenic acid is capable of uniting with lime in two different proportions, forming a seleniate and a bi-seleniate.

1121. The salts of lime which are soluble are not altered by pure ammonia, but they are decomposed by potassa and soda. They are also decomposed by the carbonates of potassa, soda and ammonia, which produce precipitates of carbonate of lime.

Oxalate of ammonia produces in their solutions a white insoluble precipitate of oxalate of lime, which, exposed to a red heat, affords pure lime.

* 3937° F. Nicholson's *Journal*, xiii. xiv.

† *Ibid*, xvii. 229.

The insoluble salts of lime are decomposed by being boiled with carbonate of potassa, and afford carbonate of lime.

SECTION VI. Barium.

1122. To obtain this metal, the earth baryta is negatively electrized in contact with mercury; an amalgam is gradually formed from which the mercury may be expelled by heat, and the metal barium remains; appearing, according to Sir H. Davy, of a dark grey colour, and being more than twice as heavy as water. It greedily absorbs oxygen, and burns with a deep red light when gently heated, producing oxide of barium. How obtain-
ed.

1123. *Oxide of Barium, Baryta, or Barya*, is obtained by exposing the crystals of nitrate of baryta for some time to a bright red heat. It may also be obtained by decomposing the native carbonate of baryta. Oxide or
Baryta,

Let this be powdered, and passed through a fine sieve. Work it up with about an equal bulk of wheaten flour into a ball, adding a sufficient quantity of water. Fill a crucible of proper size, about one third its height, with powdered charcoal; place the ball on this; and surround and cover it with the same powder, so as to prevent its coming into contact with the sides of the crucible. Lute on a cover; and expose it, for two hours, to the most violent heat that can be raised in a wind furnace. Let the ball be removed when cold. On the addition of water, it will evolve great heat, and the baryta will be dissolved. The filtered solution, on cooling, will shoot into beautiful crystals. How obtain-
ed.

1124. Baryta is of a grey colour, and very difficult of fusion; it appears to consist of 70 barium + 8 oxygen, and is, consequently, represented by 78. Its specific gravity is about 4, hence the name of *Baryta*, as being the heaviest of the substances usually called earths. It eagerly absorbs water, heat is evolved, and a white solid is formed, containing about 10 per cent. of water, which it retains at a red heat; this is the *hydrate of baryta*, and may be considered as a compound of 1 proportional of baryta = 78 + 1 proportional of water = 9, and is, consequently, represented by 87. Properties.

1125. *Hydrate of Baryta* dissolves in boiling water, and, as the solution cools, deposits regular crystals, which contain a large quantity of water, and are easily fusible. According to Mr Dalton, crystallized baryta consists of 1 proportional of baryta, and 20 of water; if it be exposed to air it effloresces into a white powder. The aqueous solution, or *baryta water*, is limpid, colourless, and acts energetically on vegetable blues and yellows, changing them to green and red; it rapidly absorbs carbonic acid, and deposits an insoluble carbonate of baryta. Hydrate.

1126. Pure baryta has a very powerful affinity for carbonic acid. Baryta wa-
ter.

Let a solution of pure baryta be exposed to the atmosphere. It will soon be covered with a thin white pellicle; which when broken, will fall to the bottom of the vessel, and be succeeded by another. This may be continued, till the whole of the baryta is separated. The effect arises from the absorption Affinity for
carbonic acid,
Exp.

of carbonic acid, which is always diffused through the atmosphere, and which forms with baryta, a substance, *viz.* carbonate of baryta, much less soluble than the pure earth.

Exp. Or if the air from the lungs be blown, by means of a quill, or tube, through a solution of baryta, the solution will immediately become milky, in consequence of the production of an insoluble carbonate. The same effect will be produced by mingling with a solution of pure baryta, a little water, impregnated with carbonic acid.

takes it from
other bodies.

1127. Baryta has so strong an affinity for carbonic acid as even to take it from other bodies. If to a solution of a small portion of carbonate of potassa, of soda, or of ammonia we add the solution of baryta, the earth will detach the carbonic acid from the alkali, and will fall down in the state of a carbonate. By adding a sufficient quantity of a solution of baryta in hot water, the whole of the carbonic acid may thus be removed from a carbonated alkali; and the alkali will remain perfectly pure. H. 1. 602.

Alkaline
properties.

1128. As baryta, like the alkalies, converts vegetable blues to green, and serves as an intermedium between oil and water, it has been called an *alkaline earth*. It has a very acrid, caustic taste, and is highly poisonous. It exists in two natural combinations only, namely, as sulphate and carbonate.

Deutoxide.

1129. When baryta is heated in oxygen, or when oxygen is passed over baryta, heated to redness in a glass tube, the gas is absorbed and a grey compound is obtained, which is the *deutoxide or peroxide of barium*; consisting of

1 proportional of barium $70 + 2$ oxygen $16 = 86$.

Thenard's
process.

1130. By dissolving peroxide of barium in muriatic acid, and precipitating by sulphuric acid, M. Thenard succeeded in obtaining the singular compound of oxygen and water, called *peroxide of hydrogen*. (405). The solution of the peroxide of barium, and the subsequent separation of the protoxide is repeated a sufficient number of times, in the same portion of dilute muriatic acid; sulphate of silver is then added to separate the muriatic acid, and the sulphuric, which then becomes its substitute, is ultimately removed by baryta. M. Thenard, in his elaborate essay upon this new compound, has shown that the process, although in theory sufficiently simple, presents many practical difficulties, chiefly arising from the impurities contained in the peroxide of barium.

1131. The following has been proposed as the most economical process for preparing the deutoxide.

Nitrate of baryta is to be put into a luted earthenware retort, to which a tube is to be attached for the purpose of conveying the liberated gases to a pneumatic trough. The retort is to be gradually heated to redness, and retained at that temperature as long as nitrous acid and nitrogen gas pass over; the evolution of these indicates that nitrate of baryta still remains to be decomposed, but the instant that pure oxygen gas passes off, the fire is to be removed and the retort cooled.

The product of this decomposition is a peroxide of barium; it falls to pieces in water, without producing heat, disengages oxygen when boiled with water, and is reduced to a protoxide

by a strong heat. In this process the protoxide formed by the decomposition of the nitrate being in contact, at a red heat, with a large quantity of oxygen in a nascent state, combines with it, and is retained, unless the heat be so high as to decompose it.*

The process then proceeds as follows.

Take a certain quantity of water (about eight ounces for instance), and add to it a sufficiency of pure and fuming muriatic acid to dissolve about 230 grains of baryta: put this acid liquor into a glass vessel, which during the operation must be surrounded by ice: then take about 185 grains of the peroxide, rub it into a fine paste with a little water in an agate mortar, and put it into the acid liquor with a box-wood spatula; it soon dissolves without effervescence: to this solution add pure sulphuric acid drop by drop, stirring it with a glass rod, till it is in slight excess, which is known by the readiness with which the sulphate falls: then dissolve a second portion of the deutoxide and precipitate as before, taking care to use enough but not too much sulphuric acid. The liquor is now to be filtered, and the residue washed with a little water, so as to keep up the original measure by adding it to the first portion: a second and third washing of the residue with very small quantities of water may be advisable, and these liquors should be kept apart for the purpose of washing the filters in subsequent operations.

A fresh portion of the peroxide is then dissolved in the filtrated liquor and decomposed as before, filtering at every two operations and washing the filter with the savings of the others. We thus proceed till the water is sufficiently oxygenated: when about two pounds of the peroxide have been consumed the water will be united to about thirty times its volume of oxygen, which is as much as it will retain, unless some muriatic acid be added, in which case M. Thenard has made it retain 125 volumes.

When the water is sufficiently oxygenated, it is retained in the ice, and supersaturated with the peroxide of barium, which occasions the separation of flocculi of silica and alumina, coloured with a little oxide of iron and of manganese; the whole is then filtered as quickly as possible, and returned into the vessel surrounded by ice, the baryta is separated by sulphuric acid, and pure sulphate of silver is added to separate the muriatic acid, upon which the liquid, before milky, becomes suddenly clear. The sulphuric acid is ultimately separated by baryta, the liquor filtered and placed in a shallow vessel, under the air-pump receiver, containing a basin of sulphuric acid; the receiver being exhausted, the water evaporates and is absorbed by the acid, while the peroxide of hydrogen being less vaporisable remains; if it give out any oxygen, which sometimes happens from its containing impurities, a drop or two of weak sulphuric acid prevents its further evolution. The properties of the peroxide of hydrogen have been already noticed.† (406.)

1132. *Chloride of Barium* may be obtained by heating baryta in chlorine, in which case oxygen is evolved: or more easily, by dissolving carbonate of baryta in diluted muriatic acid. The iron and lead, which are occasionally dissolved, along with the baryta, may be separated by the addition of a small quantity of liquid ammonia, or by boiling and stirring the solution in contact with a little lime; or which is still better, by solution of baryta in water. When filtered and evaporated, the solution yields regular crystals, which have most commonly the shape of tables, or of eight-sided pyramids applied base to base.

1133. These crystals dissolve in five parts of water, at 60°, or in a still smaller quantity of boiling water, and also in alcohol. They are not altered by exposure to the atmosphere; nor are

Chloride of
Barium.

Properties.

* *Ann. de Chim.* xxxvi. 108.

† *Hydrobromate of Baryta* fuses by heat, dissolves readily in water or alcohol. It forms crystalline mamellated masses.

they decomposed, except partially, by a high temperature. The sulphuric acid separates the muriatic; and the salt is also decomposed by alkaline carbonates and sulphates.

Composition. 1134. The dry salt Sir H. Davy considers as a compound of 1 atom of barium = 70 + 1 atom chlorine = 36, hence its representative number is 106; and it consists of chlorine 34, barium 66 = 100. By solution in water it is converted into muriate of baryta, each atom decomposing 1 atom of water. H. 1. 599.

The taste of chloride of barium is pungent and acrid; when exposed to heat, the water of crystallization separates, and the dry chloride enters into fusion.

Chlorate of Baryta.

1135. *Chlorate of Baryta*.—To prepare this salt, chlorine gas must be received into a warm solution of baryta in water, till the baryta is saturated. The solution is to be filtered, and boiled with phosphate of silver, which decomposes the common muriate of baryta, and at the same time composes two insoluble salts, phosphate of baryta and chloride of silver. Vauquelin finds the addition of acetic acid recommended by Chenevix, objectionable, and that the compounds of chloric acid are liable, if acetic acid has been employed, to detonate violently when heated. To judge when enough of the phosphate of silver has been used, add to a portion of the filtered liquor, a few drops of nitrate of silver, which, in that case, ought not to disturb its transparency. If too much phosphate of silver has been used, a drop or two of muriatic acid will discover it, and, in that case, the cautious addition must be made of some of the original solution, set apart for the purpose, to which no phosphate of silver has been added. It is from solution of chlorate of baryta, thus carefully prepared, that chloric acid is obtained by the intervention of sulphuric acid (328.) H. 1. 600. It crystallizes in quadrangular prisms, soluble in four parts of water, at 60°; and consists of

Composition. 1 atom of baryta 78, + 1 of chloric acid 76 = 154.

Its solution, when pure, is not precipitated by nitrate of silver or muriatic acid.*

Iodate.

1136. *Iodate of Baryta* may be formed by adding iodine to solution of baryta, from which the iodate precipitates in the state of a white powder, and may be edulcorated by washing with distilled water. When strongly heated it evolves oxygen and iodine, and baryta remains. It consists of 1 atom baryta + 1 iodic acid.

Hydriodate.

1137. *Hydriodate of Baryta* is extremely soluble in water and rather deliquescent. It crystallizes in very small prisms which are decomposed by mere exposure to the atmosphere, into water, a salt with excess of iodine, and carbonate of baryta. When ignited in close vessels it is converted into iodide of barium.

* *Iodide of Barium* is easily formed by acting upon baryta by hydriodic acid, and evaporating the solution. It may also be formed by heating baryta in hydriodic gas; water and iodide of barium are the results.

1138. *Nitrate of Baryta* may be prepared by dissolving the native carbonate in nitric acid,* evaporating to dryness, re-dissolving, and crystallizing; it forms octoëdral crystals.† Its taste is acid and astringent. It is soluble in 12 parts of cold and 4 of boiling water; it is decomposed by a bright red heat, furnishing pure baryta. It consists of 78 baryta + 54 nitric acid = 132. Nitrate.

If a moderately strong solution of the nitrate of baryta be added to nitric acid, a precipitation of nitrate of baryta takes place, in consequence of the abstraction of water by the acid; hence in using nitrate of baryta as a test of the presence of sulphuric acid in nitric acid, the latter should be considerably diluted previous to its application.‡ Action of nitric acid.

1139. *Hyposulphite of Baryta*.—This salt is thrown down on pouring muriate of baryta into a solution, not too dilute, of hyposulphite of lime; it is a white powder, soluble without decomposition in muriatic acid; at a low heat it takes fire and the sulphur burns off. When the solutions from which it is precipitated are dilute, it falls, after some minutes, in small crystalline grains, followed by a copious separation of the salt.§ Hyposulphite.

1140. *Sulphite of Baryta* is insoluble in water, and formed by adding sulphite of potassa to muriate of baryta. Sulphite.

1141. *Sulphate of Baryta* is an abundant natural product; it is insoluble and therefore produced whenever sulphuric acid or a soluble sulphate, is added to any soluble salt of baryta; hence the solutions of baryta are accurate tests of the presence of sulphuric acid. Sulphate of baryta consists of one proportional of sulphuric acid and one of baryta. Sulphate.

40 sulphuric acid + 78 baryta = 118.

1142. *Native Sulphate of Baryta, Heavy Spar, or Baroselenite*, is principally found in the mines of Westmoreland and Cumberland, and in Transylvania, Hungary, Saxony, and Hanover. A variety met with in Derbyshire, is called *cawk*. It occurs massive, and crystallized in a great variety of forms. Its primitive figure is a rhomboidal prism. It is harder than carbonate of lime, but not so hard as fluuate of lime. Its specific gravity is 4,7. Native sulphate.

When native sulphate of baryta is heated it decrepitates, and at a high temperature, fuses into an opaque white enamel: it was employed in the manufacture of *jasper ware* by the late Mr Wedgwood. When heated to redness, it acquires the property of phosphorescence. This was first ascertained by Vincenzo Cascariolo, of Bologna, whence the term *Bologna* Uses.

* If the artificial carbonate be employed, it should be previously well washed with distilled water, till the washings cease to precipitate nitrate of silver. A solution of nitrate of baryta mixed with one of nitrate of silver, should continue perfectly transparent. H.

† See Mr Brooke's representation of them in *Ann. Philos.* N. S. vii. 21.

‡ *Sulphuret of Barium* is a brown compound, which acts upon water producing *hydrosulphuret of baryta*.

§ Herschell, *Edin. Philos. Journal*, i. 20.

Bologna phosphorus.

phosphorus is applied to it.* This kind of phosphorus, after being exposed for a few minutes to the sun's rays, shines in the dark sufficiently to render visible the dial of a watch. This property is lost by repeated use, in consequence of the oxygenation of the sulphur; but it may be restored by a second calcination.

The artificial sulphate of baryta is used as a pigment, under the name of *permanent white*. It is very useful for marking phials and jars in a laboratory. Sulphate of baryta is sparingly soluble in sulphuric acid.

1143. As the native sulphate is a common and abundant compound, several processes have been contrived for obtaining from it pure baryta.

This may be effected by reducing the crystallized sulphate to a fine powder, and heating it red hot for half an hour in a silver crucible with three parts of carbonate of potassa,† the fused mass is then boiled repeatedly in water, till it no longer affords any thing soluble in that liquid; the insoluble residue, consisting chiefly of carbonate of baryta, may be digested in dilute nitric acid, by which nitrate of baryta is formed, and which will yield the pure earth by exposure to heat. The following method has been recommended by Dr Henry. The sulphate of baryta is to be finely powdered, mixed with three or four times its weight of carbonate of potassa, and boiled with a proper quantity of water for a considerable time, in an iron kettle, stirring it, and breaking down the hard lumps, into which it is apt to run, by an iron pestle. It is then to be washed with boiling water, as long as this acquires any taste. On the addition of dilute muriatic acid, a violent effervescence will ensue, and a considerable portion of the earth, probably along with some metals, will be dissolved. To the saturated solution, add solution of pure baryta in water, as long as it disturbs the transparency of the liquor. This will throw down any metals that may be present; and the excess of baryta may afterwards be precipitated in the state of a carbonate, by a stream of carbonic acid. Decompose the muriatic solution by any alkaline carbonate; let the precipitated earth be well washed with distilled water; and if the pure baryta is to be obtained from it, let it be treated as directed page 308.

* To prepare this substance the native sulphate, powdered after being ignited, is to be formed into a paste with mucilage of gum arabic, and divided into cylinders or pieces of one fourth of an inch in thickness. These, after being dried in a moderate heat, are to be exposed to the temperature of a wind furnace, placed in the midst of the charcoal. When the fuel is half consumed, it must be replenished, and suffered to burn out. The pieces will be found, retaining their original shapes, among the ashes, from which they may be separated by the blast of a pair of bellows. They must be preserved in a well-stopped phial. H. 1. 607.

† Sulphate of baryta is decomposed by alkaline carbonates, either by fusing a mixture of one part of the finely powdered sulphate with three of carbonate of potassa or soda, or by boiling together the pulverized sulphate and a solution of carbonate of potassa. Respecting this decomposition some curious facts have been ascertained by Dulong and by Mr R. Phillips. When sulphate of baryta is boiled, for two hours, in contact with precisely its equivalent quantity of carbonate of potassa, (that is, with the quantity which ought, from theory, to produce entire decomposition) only one fourth of the sulphate of baryta is converted into carbonate. Reversing the process, and boiling together equivalent quantities of carbonate of baryta and sulphate of potassa (the mutual decomposition of which could not have been expected from the established order of affinities) it was found that, out of 85 parts of carbonate of baryta, 57 had been changed into sulphate. It is obvious, therefore, that the entire decomposition of sulphate of baryta by carbonate of potassa can never be expected, so long as the carbonate of baryta, formed by the mutual action of these two salts, remains in contact with the sulphate of potassa generated at the same time, for this will reconvert the carbonate of baryta into sulphate. Nor will any quantity of carbonate of potassa, that can be employed, be adequate to the entire decomposition of sulphate of baryta.

By this process carbonate of baryta may, however, be procured in sufficient quantity for the purpose of preparing the pure earth and various salts, when the native carbonate cannot be had in sufficient abundance. H. 1. 606.

Methods of
obtaining
pure baryta
from native
sulphate.

Another method consists in exposing to a red heat, in an earthen crucible, a mixture of six parts of finely powdered sulphate of baryta, with one of powdered charcoal, for half an hour. This converts the sulphate into sulphuret of baryta, which is to be dissolved in hot water, the solution filtered and mixed with solution of carbonate of soda as long as it occasions a precipitate, which when washed and dried, is carbonate of baryta. Or, by adding muriatic acid to the liquid sulphuret, sulphur is thrown down and sulphuretted hydrogen evolved, and muriate of baryta formed, which may be filtered off, and if required, decomposed by carbonate of potassa. Or the sulphuret, as it comes out of the crucible, may be thrown into dilute nitric acid, by which sulphuretted hydrogen is evolved, and a nitrate of baryta formed, which may be separated from the remaining impurities by copious washings with hot water.

1144. *Phosphuret of Barium* is produced by passing phosphorus over heated baryta; there is an intense action and a phosphuret of a metallic lustre is obtained, which acts upon water, and affords a solution containing *Hypophosphite of Baryta*.*

1145. *Phosphite of Baryta* was obtained by Berzelius by adding muriate of baryta to phosphite of ammonia: a crust of phosphite of baryta was formed in 24 hours, consisting of

| | |
|------------------|-------|
| Phosphorous acid | 24,31 |
| Baryta | 67,24 |
| Water | 8,45† |

1146. *Phosphate of Baryta*.—Phosphoric acid and baryta combine in various proportions.

The first, or *neutral phosphate*, is formed by mixing solutions of muriate of baryta and phosphate of soda. An insoluble precipitate is obtained, which, whenedulcorated and dried contains, according to Berzelius

| | |
|-----------------|------|
| Phosphoric acid | 31,8 |
| Baryta | 68,2 |

100.

1147. By dissolving phosphate of baryta in phosphoric acid, and evaporating the clear solution, Berzelius obtained white crystals, which had an acid taste, and reddened vegetable blues. They are probably constituted of 2 atoms of acid + 1 of base, and may be considered as the *bi-phosphate*.

1148. When a solution of the above crystals is poured into alcohol, a bulky precipitate falls, which is white and tasteless. It appears to consist of 2 atoms of base and 3 of acid, or 1 of the former and $1\frac{1}{2}$ of the latter, and hence may be called a *sesqui-phosphate*.‡ H. 1. 604.

* *Hypophosphite of Baryta*, like the other hypophosphites, is very soluble and scarcely crystallizable.

† *Ann. de Chim. et Phys.* ii. 231.

‡ Besides the above, Berzelius has described two sub-phosphates of baryta.—*Ann. of Philos.* xv. 277.

Carbonate.

1149. *Carbonate of Baryta* is found native. Artificially produced, it is a white compound insoluble in water, containing
 $22 \text{ carbonic acid} + 78 \text{ baryta} = 100.$

It is poisonous.

Native.

1150. Native carbonate of baryta was first discovered at Anglesark, in Lancashire, by Dr Withering, and hence acquired the name of *Witherite*. It is useful as a source of pure baryta and its salts, and though not soluble in water, is poisonous. It dissolves very sparingly in solution of carbonic acid, whence the superiority of baryta water to lime water in some cases as a test of carbonic acid.

The native carbonate of baryta is much more difficult of decomposition by heat than the artificial.

Dr Henry recommends the following process.

Let the native carbonate be powdered and passed through a fine sieve. Work it up with about an equal bulk of wheaten flour into a ball, adding a sufficient quantity of water. Fill a crucible of proper size, about one third its height, with powdered charcoal; place the ball on this; and surround and cover it with the same powder, so as to prevent its coming into contact with the sides of the crucible. Lute on a cover; and expose it, for two hours, to the most violent heat that can be raised in a wind furnace. Let the ball be removed when cold. On the addition of water, it will evolve great heat, and the baryta will be dissolved. The filtered solution, on cooling, will shoot into beautiful crystals.

Seleniate.

1151. *Seleniate of Baryta*. Selenic acid is capable of uniting with baryta in two proportions. The neutral salt, which is insoluble, consists of 100 acid + 137,7 base; the *biseleniate* which crystallizes in round transparent grains, and is soluble in water, is composed of 100 acid + 68 base.*

Ferro-cyanate.

1152. *Ferro-cyanate of Baryta* may be formed by adding Prussian blue to a heated solution of baryta in water, till it ceases to be discoloured. The filtered solution deposits yellowish crystals, which have the figure of rhomboidal prisms, and are soluble in 1920 parts of cold, or 100 parts of boiling water. They dissolve in nitric and muriatic acids. They consist of

| | |
|-----------------|-------|
| Acid | 34,31 |
| Base | 49,10 |
| Water | 16,59 |

100. H. 1. 608.

Characters of
the salts of
baryta.

1153. The soluble barytic salts furnish white precipitates of carbonate and sulphate of baryta, upon the addition of carbonate or sulphate of soda. They give a yellow tinge to the flame of spirit of wine. The sulphate is insoluble in nitric acid and in the alkalies.

Nearly all the barytic compounds are poisonous; the safest antidote is solution of sulphate of soda, or dilute sulphuric acid.† The muriate of baryta has been employed in medicine, but the principal use of baryta is in the chemical laboratory. It is possible that pure baryta might be economically used for the decomposition of sulphate of soda, to obtain the pure alkali.

* *Borate of Baryta* is an insoluble white powder.

† Orfila, *Traité des Poisons*, Tom. i. 2me, p. 167.

SECTION VII. *Strontium.*

1154. This metal is procured from the earth strontia by the same process as barium, which metal it resembles in appearance.

1155. *Protoxide of Strontium*, or the earth *Strontia*, is so called from Strontian in Scotland, where it was first discovered in combination with carbonic acid. It may be prepared either by subjecting the carbonate to a strong heat in a crucible, or by igniting the nitrate in a porcelain retort or other close vessel. A grey substance remains which becomes very hot on the affusion of water; and when more water is added and heat applied, a considerable proportion of the earth is dissolved. On cooling, the solution deposits regular crystals; but the shape of these differs considerably from that of barytic crystals. The crystals of strontia are thin quadrangular plates, sometimes square, oftener parallelograms. Their primary form is a right square prism.* H. 1. 609.

Strontia.

How obtained.

1156. According to Stromeyer, Strontia consists of 1 proportional Strontium 44 + 1 oxygen 8 = 52.

Composition.

1157. Pure strontia has a pungent, acrid taste, and when powdered in a mortar, the dust that rises irritates the lungs, and nostrils. Its specific gravity approaches that of baryta. It requires about $51\frac{1}{2}$ parts of water at 60° for solution, but boiling water takes up half its weight. On cooling, the crystals separate.

Properties.

1158. The crystals of strontia give a blood red colour to the flame of burning charcoal. The solution of strontia changes the vegetable blues to a green.

1159. Strontia does not combine with alkalies. Baryta has no affinity for it, for no precipitation ensues on mixing the watery solutions of the two earths. H.

1160 *Chloride of Strontium* may be formed either by heating strontia in chlorine gas which disengages oxygen; or by dissolving carbonate of strontia in muriatic acid and evaporating to dryness. It consists of 1 proportional strontium 44 + 1 of chlorine 36 = 80.

Chloride.

1161. The chloride may be converted into *muriate* by the action of water. It crystallizes in long, slender hexagonal prisms, which are soluble in two parts of water at 60° and to almost any amount in boiling water. In a very moist atmosphere they deliquesce. They dissolve in alcohol and communicate to its flame a blood red colour.†

Muriate.

* Brooke in *Ann. of Philos.* N. S. vii. 287.

† *Chlorate of Strontia* may be obtained by the direct action of chloric acid on carbonate of strontia. It is a deliquescent salt, having an astringent taste. It detonates when thrown upon red-hot coals with a beautiful purple light.

Chlorate.

Iodide of Strontium may be formed as iodide of barium (p. 268). Dissolved in water, and carefully evaporated, it furnishes delicate prismatic crystals of *Hydriodate of Strontia*, which, heated in close vessels, fuses, and becomes iodide of strontium by loss of water.

Iodide.

Iodate of Strontia is a very difficultly soluble compound; it is resolved at a red heat into oxygen, iodine and strontia.

Nitrate.

1162. *Nitrate of Strontia* may be obtained in the same manner as the nitrate of baryta. Its taste is pungent and cooling.* Its crystals are dissolved by their own weight of water at 60° , or by little more than half their weight of boiling water. When applied to the wick of a candle, or added to boiling alcohol, they communicate to the flame a deep blood red colour. They are decomposed by a high temperature, and afford pure strontia. Exclusive of water, the salt consists, according to Stromeyer, of 50,62 acid + 49,38 base.† H. I. 611.

Sulphuret of Strontium.

1163. *Sulphuret of Strontium* may be formed by fusing 3 parts of dry strontia and 1 of sulphur in a green glass tube; or by exposing the powdered sulphate to a red heat with charcoal. It dissolves in water with the same phenomena as sulphuret of potassa, and its solution furnishes, by cautious evaporation, crystals of *hydrosulphuret of strontia*.

Hyposulphite of Strontia.

1164. *Hyposulphite of Strontia* is formed by passing sulphurous acid into the liquid sulphuret: it crystallizes in rhomboids permanent at common temperatures and soluble in about $1\frac{3}{4}$ times its weight of water. According to Mr Herschel, this salt is doubly refractive. Its taste is bitter, and it is insoluble in alcohol.

Sulphate.

1165. *Sulphate of Strontia* occurs native. It is nearly insoluble, 1 part requiring 4000 of water for its solution. (3840 boiling. H.) When heated with charcoal, its acid is decomposed, and *sulphuret of strontia* is formed, which affords nitrate by the action of nitric acid. This process equally practicable upon sulphate of baryta (1013), is sometimes adopted to obtain the earth. Sulphate of strontia dissolves in hot sulphuric acid, but is thrown down upon adding water. It consists of

55 Strontia + 40 Acid.‡

Native.

1166. The *Native Sulphate of Strontia* is sometimes of a blue tint, and has hence been called *celestine*. Sometimes it is colourless and transparent. Fine crystallized specimens are accompanied with native sulphur, from Sicily.

Magnificent crystals are found on Strontian Island in Lake Erie.§ || Its specific gravity is 3,2. As the native carbonate

* This salt is used in the *red fire* employed at the theatres, which consists of 40 parts of dry nitrate of strontia, 13 powdered sulphur, 5 of chlorate of potassa, and 4 of sulphuret of antimony. The chlorate and sulphuret should be separately powdered, and mixed together on paper with the other ingredients; a very small quantity of powdered charcoal may also be added.

† The forms of the crystals, and also of another variety which is anhydrous, have been given by Mr Brooke in *Ann. of Philos.* N. S. vii. 288.

‡ According to a considerable majority of the chemists who have analyzed it, sulphate of strontia consists of

| | | | | | | | | | | | |
|----------|---|---|---|---|---|----|---|---|---|---|-----|
| Acid | - | - | - | - | - | 42 | - | - | - | - | 100 |
| Strontia | - | - | - | - | - | 53 | - | - | - | - | 138 |
| | | | | | | | | | | | |
| | | | | | | | | | | | 100 |
| | | | | | | | | | | | 238 |

From these numbers its equivalent has been deduced by Dr Wollaston. But Vauquelin has stated, that it is composed of 46 acid and 54 base, and Stromeyer of 43 acid and 57 base. The theoretical constitution of 1 atom of acid + 1 of base would require it to consist of 43,47 acid + 56,53 of base. II.

§ Discovered by Major Jas. Delafield. See *Amer. Jour. of Science*, vol. iv. p. 279.

|| *Hypophosphite of Strontia* has been examined by Dulong: it is a very soluble and difficultly crystallizable salt.

is rather scarce, this compound may be advantageously employed for procuring artificial carbonate of strontia. The process is precisely similar to that for decomposing the sulphate of baryta.

1167. *Phosphate of Strontia* may be formed by mixing solutions of muriate of strontia and phosphate of soda. It is insoluble in water, but soluble in an excess of phosphoric acid; it is fusible by the blow-pipe into a white enamel, and decomposable by sulphuric acid. By igniting it with charcoal, *phosphuret of strontium* is obtained. It consists of 1 proportional of strontia + 1 of acid.* B. Phosphate.

1168. *Carbonate of Strontia*.—The relation of strontia to carbonic acid resembles, very nearly, that of baryta, and similar experiments may be made with its solution. Carbonate.

1169. Carbonate of strontia is found native, and was first discovered in 1787 at Strontian in Scotland, whence the name of this earth.† Discovery.

1170. The *native* carbonate of Strontia has a greenish tint, and occurs in radiated masses, and sometimes in acicular and hexaëdral crystals. Its specific gravity is 3,6. Native.

1171. The carbonate of strontia requires for solution 1536 parts of boiling water. The artificial carbonate, according to Stromeyer‡ does not essentially contain any water. It consists of Properties and composition.

| | | |
|-------------------|---------------|-------|
| Strontia | 70,313 or 100 | |
| Carbonic acid . . | 29,687 | 42,22 |
| 100. | | |

These scarcely differ from its theoretical proportions, *viz.* 1 proportional strontia 52, + 1 carbonic acid 22 = 74.

When strongly heated with charcoal powder, it is decomposed, carbonic oxide is given off, and pure strontia remains.§

1172. There is in many respects a resemblance between strontia and baryta which has led to confusion in analysis.

The following are some of the most striking points of resemblance. They are both found native in the states of sulphate and carbonate only; both sulphates are soluble in excess of sulphuric acid, and nearly insoluble in water; they are decomposable by similar means, as well as the native carbonates: they are both crystallizable from their hot aqueous solutions, and both attract carbonic acid. The carbonates are each soluble with effervescence in most of the acids; but the native carbonates are not so easily acted on as the artificial. Pure ammonia precipitates neither one nor the other. Points of resemblance between strontia and baryta.

* According to Stromeyer it consists of Acid 36,565
Base 63,435

100.

† It was first examined by Professor Hope of Edinburgh in 1791. His experiments are detailed in the *Philosophical Transactions of the Royal Society of Edinburgh*, vol. iv. p. 44.

‡ *Ann. de Chim. et Phys.* iii. 396.

§ *Borate of Strontia* was formed by Dr Hope. It is a white powder, soluble in 130 parts of water.

Distinctions.

The following are essential distinctions. Baryta and all its salts, except the sulphate, are poisonous. The corresponding strontitic salts are innocent. Baryta tinges flame yellow; strontia, red. Strontia has less attraction for acids than baryta, hence the strontitic salts are decomposed by baryta. The greater number of the barytic salts are less soluble than those of strontia, and they differ in their respective forms and solubilities. Pure baryta is ten times more soluble in water than pure strontia. Baryta forms with silicated fluoric acid a crystalline insoluble precipitate, but strontia forms with it a very soluble fluuate of strontia and silica.*

SECTION VIII. *Magnesium.*

1173. The metallic base of magnesia has not hitherto been obtained; but, when that earth is negatively electrized with mercury, the resulting compound decomposes water, and gives rise to the formation of *magnesia*. From the properties of the amalgam it appears that it is a white solid metal heavier than water, and highly attractive of oxygen.

Magnesia.

1174. *Magnesia or Oxide of Magnesium* is concluded, from indirect experiments, to consist of 12 metal + 8 oxygen; its representative number, therefore, is 20. It may be procured by exposing the carbonate of magnesia to a red heat. Magnesia is a white insipid substance, which slightly greens the blue of violets. Its specific gravity is 2,3; it is almost infusible and insoluble in water. Prof. Brande once succeeded in agglutinating a small portion of this earth in the voltaic flame, and whilst exposed to this high temperature, it was perfectly fused by directing upon it the flame of oxygen and hydrogen. A mixture of magnesia and lime is scarcely more fusible than the pure earth. It does not absorb carbonic acid or moisture, as is the case with the other alkaline earths.

Magnesia is by no means a rare production of nature, for though very seldom found in a state approaching to purity, yet it enters largely into some rocks that compose extensive formations, such as serpentine, steatite, &c.: and in combination with sulphuric and muriatic acids it forms a large proportion of the ingredients of sea-water. Its principal use is in medicine.

Native Hydrate.

1175. *Native Hydrate of Magnesium* is found at Hoboken, in New Jersey, its colour is white inclining to green; its texture lamellar and soft. It is dissolved in acids without effervescence, and consists of 70 magnesia, 30 water.

Chloride.

1176. *Chloride of Magnesium* may be obtained by passing chlorine over red-hot magnesia; oxygen is expelled, and a sub-

* *Ann. de Chim.* xxvii. 301,

stance obtained which moisture converts into muriate of magnesia.

1177. *Chloride of Magnesia* may be prepared by passing Chloride. chlorine gas into water, in which magnesia is kept mechanically suspended, or by the mixture of solutions of chloride of lime and sulphate of magnesia.

It is of use in some of the processes of bleaching and calico Uses. printing. H. 1. 615.*

1178. *Muriate of Magnesia* is very deliquescent, and difficultly crystallized. Its solution has a bitter saline taste. Exposed to heat and air, muriatic acid flies off and the magnesia remains pure. It consists of 1 atom muriatic acid, 1 magnesia and 5 atoms water. Muriate,

1179. *Muriate of Magnesia* is found in a few saline springs, in sea-water. and constitutes about one eighth of the solid ingredients of the water of the ocean.† By evaporating a pint of sea-water we obtain

| | | | |
|------------------------------|---------------------------------|----------|---------------------------|
| Common Salt . . . 180,5 grs. | Sulphate of Magnesia . . . 15,5 | } 226,1† | Other salts in sea-water. |
| Muriate of Magnesia 23 | Sulphate of Lime 7,1 | | |

The average specific gravity of sea-water is 1,026 or 1,028. It freezes at about 28,5°, and does not appear materially to differ in composition in different latitudes, provided it be taken from a sufficient depth. Near the mouths of rivers, and in the vicinities of melting ice or snow, its composition will of course vary.‡

1180. *Hydriodate of Magnesia* is deliquescent and abandons Hydriodate. its acid when heated. When *iodine* is heated along with magnesia and water, both hydriodate and iodate of magnesia are formed. By concentrating the solution, both salts are partly decomposed; and a flocculent *iodide of magnesia* is formed, Iodide. which when heated, loses part of its iodine, and is changed into a sub-iodide. H. 1. 616.

1181. *Nitrate of Magnesia* may be prepared by dissolving Nitrate. carbonate of magnesia in diluted nitric acid. The solution, when evaporated, yields crystals in the shape of prisms, with four oblique faces truncated at their summits. Most commonly, however, it forms a shapeless mass, consisting of an immense number of small needle-shaped crystals, crossing each other irregularly. These crystals deliquesce in the air, and are soluble in half their weight of water. When exposed to the heat of ignition, they fuse; a few bubbles of oxygen gas first escape; and the nitric acid then passes undecomposed. The salt contains, according to Thomson, 1 atom of nitric acid, 1 of magnesia and 6 atoms of water.

* *Hydromate of Magnesia* is deliquescent and uncrystallizable, and is decomposed by an elevated temperature.

† *Philos. Trans.* 1810.

‡ *Murray's Analysis of Sea-Water, Edinburgh Phil. Trans.* vol. viii. p. 205.

§ *Chlorate of Magnesia* is a bitter deliquescent salt.

Ammonio-
Nitrate.

1182. *Ammonio-Nitrate of Magnesia* may be obtained by evaporating a mixed solution of nitrate of ammonia and nitrate of magnesia; it forms prismatic crystals of a bitter acrid taste, soluble in about 11 parts of water at 60°, and less deliquescent than their component salts separately.*

Sulphuret.

1183. *Sulphuret of Magnesia*.—Sulphur and magnesia do not appear to form a complete sulphuret, for when melted together the compound does not dissolve in water; and when heated the sulphur burns off.†

Hypsul-
phite.

1184. *Hypsulphite of Magnesia* may be formed by boiling flowers of sulphur in solution of sulphite of magnesia; it is bitter, very soluble, but not deliquescent. Being more soluble in hot than cold water, it readily crystallizes as its solution cools; heated, it burns with a blue flame, and by a sufficient continuance of the heat, the whole of the acid is expelled, and magnesia remains.‡

Sulphate.

1185. *Sulphate of Magnesia* is a commonly occurring compound of this earth, much used in medicine as an aperient.§ It is largely consumed in the preparation of carbonate of magnesia. The primary form of the crystals is a right prism with a rhombic base. Its taste is bitter. It is soluble in its own weight of water at 60°. When exposed to a red heat, it loses its water of crystallization, amounting to about 50 *per cent.*, but is not decomposed. It consists of

Composition.

Magnesia . . . 20 . . . Sulphuric acid 40 = 60.

In its crystallized state, it may be considered as composed of 1 proportional of dry sulphate + 7 proportionals of water, or 60 sulphate + 63 water = 123.

How obtain-
ed.

1186. This salt is usually obtained from sea-water, the residue of which, after the separation of common salt, is known by the name of *bittern*, and contains sulphate and muriate of magnesia; the latter is decomposed by sulphuric acid: a portion of muriate of magnesia often remains in the sulphate and renders it deliquescent: it is also occasionally obtained from saline springs; and sometimes by the action of sulphuric acid on magnesian limestone. It was once procured from the springs of Epsom in Surrey, and hence called *Epsom salt*. It has been found native, constituting the *bitter salt* and *hair salt* of mineralogists: it not unfrequently occurs as a fine capillary incrustation upon the damp walls of cellars and new buildings.

Epsom salt.

* Fourcroy, *Annales de Chimie*, iv. 215.

† *Hydro sulphuret of Magnesia*.—Magnesia is soluble in water imptegated with sulphuretted hydrogen, but the properties of the compound have not been investigated. H.

Sulphite.

‡ *Sulphite of Magnesia* is prepared by passing sulphurous acid through water containing diffused magnesia. It forms tetraëdral crystals soluble in 20 parts of water at 60°.

§ When highly concentrated sulphuric acid is suddenly added to fresh prepared and pure magnesia, very great heat and vapour are excited, accompanied frequently with an extrication of light: an appearance first observed by Westrumb. But if the carbonate of magnesia be added to diluted sulphuric acid, the carbonic acid is expelled, and a solution of sulphate of magnesia is formed, which crystallizes on evaporation and cooling. H.

1187. The sulphate of magnesia of commerce is occasionally adulterated with small crystals of sulphate of soda; the fraud is detected by the inferior weight of the precipitate, occasioned by adding carbonate of potassa; 100 parts of pure crystallized sulphate of magnesia furnishing a precipitate of about 40 parts of dry carbonate.*

Adulteration,
how detected.

1188. *Ammonio-Sulphate of Magnesia* may be obtained by pouring ammonia into a solution of the sulphate of magnesia, in which case, part only of the magnesia is thrown down, the remainder forming with the sulphate of ammonia this triple salt. It consists of 60 sulphate of magnesia, 56 sulphate of ammonia and 63 water.†

Ammonio-
Sulphate.

1189. *Phosphate of Magnesia* is formed by adding the carbonate of magnesia to phosphoric acid; or by mixing solutions of phosphate of soda and sulphate of magnesia; no immediate change ensues, but, after a few hours large transparent crystals of phosphate of magnesia make their appearance in the solution. The crystals require 15 parts of cold water‡ but a smaller proportion of boiling water, for solution. They effloresce in the air, and, when heated, leave a dry powder, which is fusible into a transparent glass. They are constituted of 1 atom of acid, 1 of base, and 7 of water.§ H. 1. 619.

Phosphate.

1190. *Ammonio-phosphate of Magnesia* is formed by mixing the solutions of phosphate of ammonia, and phosphate of magnesia; on any other soluble salt with base of that earth. It falls down in the form of a white insoluble powder; but, in certain varieties of urinary calculi, it is found lining cavities of the concretions, in a distinctly crystallized form, and it is deposited in crystals on the sides of vessels in which urine is long kept. It is tasteless, and scarcely soluble in water, but readily soluble in dilute acids. Exposed to a high temperature it falls into powder, evolves ammonia, and fuses with difficulty. According to Fourcroy, it contains equal weights of phosphate of ammonia, phosphate of magnesia, and water.||

Ammonio-
phosphate.

* Much of the sulphate found in the shops contains some muriate of magnesia, which renders it deliquescent, and consequently, it requires to be preserved in close covered jars. It is often adulterated with Glauber's salt, which is made to resemble Epsom salt, by stirring it briskly, when it is about to crystallize. It may be detected by precipitating the magnesia by pure ammonia, aiding by heat; filtering and evaporating the filtered fluid to dryness by a heat sufficient to volatilize the sulphate of ammonia; if it contains Glauber's salt the soda will remain fixed. Or it may be detected by no precipitation ensuing, on adding carbonate of potassa to the solution. Muriate of lime is detected by the oxalic acid.—Thomson's *Lond. Disp.* 407.

† Thomson.

‡ According to late experiments of Mr Graham one grain of the anhydrous phosphate requires for solution 744 grains of water at 45° F. and 1151 grains of boiling water.—Brewster's *Jour.* xiv. 381.

§ Thomson.

|| To separate magnesia from other earths, Dr Wollaston availed himself of the formation of this triple phosphate. A mixture, for instance, of lime and magnesia may be dissolved in muriatic acid; and, upon the addition of bi-carbonate of ammonia, the lime is thrown down in the state of carbonate, but the magnesia is retained by the excess of carbonic acid. Filter and add a saturated solution of phosphate of soda, and in a short-time the ammonio-magnesian phosphate falls down, 100 grains of which are equivalent to about 20 of magnesia. In occasionally employing this process, however, I have never been able to throw down the whole of the magnesia, a portion being under all circumstances retained in solution.—Brande.

Dr Wollas-
ton's method
of separating
magnesia.

Carbonate.

1191. *Carbonate of Magnesia*.—Pure magnesia does not attract carbonic acid with nearly the same intensity as lime. Hence magnesia may be exposed to the air without any important change in its properties, or much increase of weight, unless the exposure be long continued, when it first becomes a hydrate by absorbing water, and then attracts carbonic acid from the atmosphere.

Process for obtaining.

The carbonate of magnesia of the shops is prepared by mixing together concentrated and hot solutions of carbonate of potassa and sulphate of magnesia. The sulphate of potassa thus formed is removed by copious washing with water, and the carbonate of magnesia is then dried. The proportions employed are filtered solutions of 4 parts of the crystallized sulphate and 3 of the carbonate of potassa. One hundred parts of the desiccated sulphate give about 71 of carbonate of magnesia, or about 33 of the pure earth. It is a white, insipid, and insoluble powder.*

1192. In this state it is not entirely saturated with carbonic acid. Its composition varies, as it has been precipitated with or without heat. If the former, it contains according to Bucholz, 42 base, 35 acid, 23 per cent. water; if prepared from cold solutions of carbonate of soda and sulphate of magnesia, it consists of 33 base, 32 acid and 35 water. Mr Dalton states it to be composed of 43 base, 40 acid, and 17 water. Berzelius is of opinion that it is a compound of 3 atoms of carbonate of magnesia with 1 atom of the quadro-hydrate of the same earth.† The true carbonate of magnesia, consisting of 1 atom of acid + 1 of base, is a natural product, and, being entirely without water, may be called the *anhydrous carbonate of magnesia*. It is found in India.

Decomposed by acids and heat.

1193. Water at 60° dissolves only 1-2493d of its weight, and at the boiling temperature, 1-9000th part, of common carbonate of magnesia.‡ The addition of almost any acid to the carbonate expels its acid, and a compound remains of magnesia with the new acid which has been added. The affinity of carbonic acid appears, indeed, to be feeble, for it is expelled by a very moderate heat, much inferior to that required for the decomposition of carbonate of lime. The residue is pure magnesia, which, for medical and chemical uses, is always prepared by the calcination of the carbonate, and hence its name of *calcined magnesia*. H. 1. 619.§

* Sulphate of Potassa and Magnesia forms rhomboidal crystals, scarcely more soluble than sulphate of potassa, and of a bitter taste. It exists in sea-water.

† T. *First Prin.* ii. 303.

‡ *Edin. Philos. Jour.* v. 305.

§ When the common carbonate is calcined in the large way, it appears as if boiling, from the extrication of carbonic acid; a small portion ascends like a vapour, and is deposited in a white powder on the cold bodies with which it comes into contact; and in a dark place, toward the end of the operation it shines with a bluish phosphoric light.

As the magnesia of the shops is sometimes adulterated with chalk, this may be detected by the addition of a little sulphuric acid diluted with eight or ten times its weight of water, as this will form with the magnesia a very soluble salt, while the sulphate of lime will remain undissolved. Calcined magnesia should dissolve in this dilute acid without any effervescence. Gypsum is detected by boiling

1194. Carbonate of magnesia was first used in medicine early in the last century. It is often obtained from sea-water, after the separation of its common salt. It is found *native* constituting the mineral called *magnesite*. It has been found at Hoboken, New-Jersey, in veins in a serpentine rock, accompanying the native hydrate. It is generally white and friable, and in some places in fine acicular crystals. Native.

1195. The saturated carbonate of magnesia (as it has generally been considered,) may be obtained, by passing streams of carbonic acid gas through water, in which common magnesia is kept mechanically suspended, or by adding a very dilute solution of carbonate of soda, highly charged with carbonic acid under pressure, to a dilute solution of sulphate of magnesia. No immediate precipitation ensues, but, after a few days, congeries of crystals will be found adhering to the inner surface of the glass vessel. According to Berzelius these crystals consist of 29,583 base, 31,503 acid, 38,914 water. Dr Henry conceives their true composition to be as follows, and that the existence of a *bi-carbonate of magnesia** has not been proved, *viz.* Saturated carbonate.

| | | |
|-----------------------------------|--------------|-----------------|
| 1 atom of magnesia | 20 | 28,60 |
| 1 atom of carbonic acid | 22 | 32, |
| 3 atoms water | 27 | 39,40 |
| | 69 | 100. H. 1. 618† |

1196. The salts of magnesia are for the greater part soluble in water, and afford precipitates of magnesia, and of carbonate of magnesia, upon the addition of pure soda, and of carbonate of soda. Phosphate of soda occasions no immediate precipitate when added to a magnesian salt, but the addition of ammonia causes a white precipitate of the triple ammonio-magnesian phosphate. Characters of the salts of magnesia.

1197. The minerals which contain magnesia are generally soft and apparently unctuous to the touch; they have seldom either lustre or transparency, and are generally more or less of a green colour.

a portion of the magnesia in distilled water, and adding to the solution mutiate of baryta, which will produce an insoluble precipitate, if gypsum be present.

* *Magnesia water*—*Liquid magnesia*; is prepared by adding three drachms of carbonate of magnesia to one gallon of water; the liquid is then impregnated with carbonic acid by means of a forcing pump. (*U. S. Pharmacop*)

† *Borate of Magnesia* may be formed artificially. It occurs native in a mineral called *boracite*, *Borate*, hitherto only found in the dutchy of Luneburgh. This is composed of 2 atoms boracic acid + 1 of magnesia or is a *bi-borate*. *T. First Prin.* ii. 304.

Carbonate of Magnesia and Potassa.—Berzelius has described a salt with double base, which may be formed by mixing bi-carbonate of potassa in excess, with muriate of magnesia†. No precipitate appears, but in a few days the salt arranges itself in crystalline groups on the sides of the vessel. It consists of Carbonate of magnesia and potassa.

| | |
|-------------------------|-------|
| Potassa - - - - - | 18,28 |
| Magnesia - - - - - | 15,99 |
| Carbonic acid - - - - - | 34,49 |
| Water - - - - - | 31,24 |

100,

† *Edin. Philos. Jour.* ii. 67.

Separation of
magnesia and
lime.

1198. The separation of magnesia and lime is a problem of some importance in analytical chemistry, as they often exist together in the same mineral, more especially in the varieties of magnesian limestone. When solution of carbonate of ammonia is added to the mixed solution of lime and magnesia in nitric or muriatic acids, carbonate of lime falls, and the magnesia is retained in solution and may be separated by boiling: this method, however simple, is not susceptible of great accuracy, for a portion of carbonate of lime will always be retained along with the magnesia in solution, and a triple ammoniac-magnesian salt is also formed. The following process is recommended by Professor Brande. To the mixed solution of lime and magnesia add oxalate of ammonia slightly acid, collect the precipitate, wash and dry it: 65 parts indicate 28 of lime. If nitric or muriatic acid were used for solution, the magnesia may afterwards be obtained by evaporation and heating the residue to redness in a platinum crucible till it ceases to lose weight. If sulphuric acid were the solvent, the same operation affords dry sulphate of magnesia of which 60 parts are equivalent to 20 magnesia.*

SECTION IX. Aluminum.

Aluminous
minerals.

Aluminum.

1199. The earth alumina constitutes some of the hardest gems, such as the sapphire and ruby; and combined with water, it gives a peculiar softness and plasticity to some earthy compounds, such as the different kinds of clay.—The experiments of Sir H. Davy afforded a strong presumption that alumina is a metallic oxide; but its base, *aluminum*, he did not obtain in such a state as to make its properties an object of investigation. Yet alloys were formed which gave sufficient evidence of its existence, and the presence of oxygen in alumina was proved, by its changing potassium into potassa, when ignited with that metal.†

* For the processes recommended by Mr R. Phillips, Dr Daubeny and others, see *Analysis of Minerals*.

† There can be little doubt of the existence of silicium and aluminum, as well as of calcium, and probably magnesium, in some of the varieties of cast-iron and steel. By fusing highly carburetted steel with alumina, a peculiar alloy results, which is white, granular, and brittle, and which yields on analysis 6.4 per cent alumina. On fusing 67 parts of this alloy with 500 of steel, a compound is obtained, which possesses all the characters of the best Bombay wootz; and, like it, when its surface is polished and washed over with dilute sulphuric acid, exhibits the striated appearance called *damask*, for which the celebrated sabres of Damascus are remarkable, and which renders it probable that they also are made of wootz. (*Quarterly Journal of Science and Arts*, ix.). Many of the varieties of cast-iron afford lime and silica when dissolved in acids, and it is highly probable that those substances as well as the alumina in the wootz, exist combined with the iron in their deoxidized or metallic state. B.

1200. It has been lately announced* that M. Oersted has succeeded in obtaining aluminum by the following process. Pure alumina was heated to redness and then intimately mixed with powdered charcoal, the mixture was introduced into a porcelain tube, and when at a red heat, dry chlorine gas was passed over it. The charcoal reducing the alumina, the metal combined with the chlorine, and oxide of carbon was also formed. The chloride of aluminum obtained being mixed with an amalgam of potassium and heated, chloride of potassium was formed, and the metal of the alumina combined with the mercury. The amalgam quickly oxidized by exposure to the air. Being distilled out of the contact of the air the mercury was volatilized, and a metallic button was left which had the colour and splendour of tin.

Oersted's
process for
obtaining
alumina.

1201. *Aluminum and Oxygen—Alumina.*—To obtain pure alumina we dissolve alum in 20 times its weight of water, and add to it a little of the solution of carbonate of soda, to throw down any iron which may be present. We then drop the supernatant liquid into a quantity of the water of ammonia, taking care not to add so much of the aluminous solution as will saturate the ammonia. The volatile alkali unites with the sulphuric acid of the alum, and the earthy basis of the latter is separated in a white spongy precipitate. This must be thrown on a filter, washed by repeated affusions of water, and then dried. Or if an alum, made with ammonia instead of potassa, as is the case with some French alums, can be got, simple ignition dissipates its acid and alkaline constituents, leaving pure alumina. U. 147.†

Alumina,
how obtain-
ed.

1202. Alumina is destitute of taste and smell. When moistened with water, it forms a cohesive and ductile mass, susceptible of being kneaded into a regular form. It is not soluble in water; but retains a considerable quantity, and is, indeed, a hydrate, containing when dried at the temperature of the atmosphere, almost half its weight of water. Even after ignition, alumina has such an affinity for moisture, that it can hardly be placed on the scale, without acquiring weight. Berzelius found, that 100 parts of alumina, after being ignited gained $15\frac{1}{2}$ from a dry atmosphere, and 33 from a humid one. For full saturation, 100 grains of alumina, he ascertained, require 54 of water.‡ It does not affect vegetable colours. It is dissolved by the liquid fixed alkalies, and is precipitated by acids unchanged. In ammonia it is very sparingly soluble. It is not soluble in alkaline carbonates.

Properties.

Baryta and strontia combine with alumina, both by fusion, and in the humid way. In the first case the result is a greenish or bluish coloured mass. In the second two compounds are formed. The first containing an excess of alumina, is in the

* Hensman's *Repertoire de Chimie*, &c.

† Gay-Lussac, *Ann. de Chim. et Phys.* v. 101.

‡ *Ann. de Chim.* lxxxii. 14.

Effect of
heat.

state of an insoluble powder; the other, having an excess of the alkaline earth, remains in solution.

1203. Alumina has the property of shrinking considerably in bulk, when exposed to heat. On this property was founded the *pyrometer* of Mr Wedgwood, designed to measure high degrees of heat by the amount of the contraction of regularly shaped pieces of china clay.* This instrument, however, is not an accurate measurer of heat, since the contraction of clay is influenced not merely by the degree of heat to which it is exposed, but by the mode of its application.

Equivalent
number.

1204. From indirect experiments, Sir H. Davy derived 24 as the number representing alumina, from which, deducting one atom of oxygen = 8, we obtain 16 for the equivalent of aluminum. The number for the equivalent of alumina, deduced by Gay-Lussac,† is 21,611, oxygen being 10; = 17,28, when hydrogen is taken as the decimal unit. Dr Thomson‡ from recent experiments, concludes it to be 2,25, oxygen being 1; = 18 when hydrogen is made unity. The former determination would reduce the atom of aluminum to 9,28, and Dr Thomson's to 10, the atom of oxygen being considered as 8.

Muriate of
alumina.

1205. *Muriate of Alumina* may be formed by dissolving fresh prepared alumina in muriatic acid, but the acid is always in excess. It is scarcely possible to obtain this salt in crystals, for by evaporation it becomes a thick jelly. It is extremely soluble in water, and when dried deliquesces. At a high temperature it abandons its acid.

Nitrate.

1206. *Nitrate of Alumina* may be formed in the same manner as the last mentioned compound, substituting nitric acid. The solution which is always acid, crystallizes in thin ductile plates. The crystals are extremely soluble, and deliquescent. When dried by pressure between folds of blotting paper, Dr Thomson finds them to consist of 1 atom of nitric acid, 2 atoms of base, and 10 of water. By a stronger heat it loses a portion of its acid.§ H. I. 631.

Alum.

1207. One of the saline combinations of alumina is of important use in the arts, namely, *alum*;|| a *triple sulphate of alumina and potassa*. This salt is usually prepared by roasting and lixiviating certain clays containing pyrites; to the leys, a certain quantity of potassa is added, and the triple salt is obtained by crystallization.¶

Alum has a sweetish astringent taste. It dissolves in 5 parts of water at 60°, and the solution reddens vegetable blues; hot

* For a description of this instrument see *Henry's Chemistry*. † *Ann. de Chim. et Phys.* xvi. 36.

‡ *Ann. of Philos.* N. S. iii. 168, and *T. First Prin.* 1. 310.

§ For a more particular account of the nitrates of alumina, see Thomson's *First Principles*, vol. 2.

|| When alumina and sulphuric acid form a triple salt with some other salifiable base instead of potassa, the compound is also called alum, but the name of that base is also prefixed to it. Thus ammoniacal alum is the sulphate of alumina and ammonia; soda alum is the sulphate of alumina and soda.

¶ Sulphate of alumina will not crystallize; but if a solution of sulphate of potassa be added to solution of sulphate of alumina, small octoëdral crystals of alum are precipitated.

water dissolves $\frac{3}{4}$ ths of its weight. It furnishes octoëdral crystals. In its crystalline form it consists, according to some recent experiments made by Mr R. Phillips, of

| | |
|--|-----|
| 2 atoms of Sulphate of alumina | 134 |
| 1 atom of Bi-sulphate of potassa | 122 |
| 25 atoms of Water | 225 |
| | — |
| | 487 |

Composition.

Dr Thomson does not admit that bi-sulphate of potassa exists in alum, and contends that it is constituted of 1 atom of sulphate of potassa, 3 atoms of sulphate of alumina, and 25 atoms of water.*

1208. When alum is exposed to an intense heat, it loses water, and a portion of acid; but the whole of the acid cannot be expelled. It becomes light and spongy; and in this state is called in the *Pharmacopœia*, *Alumen ustum*, or *exsiccatum*. If alum contain excess of potassa it forms cubic crystals, and is known under the name of cubic alum.

Alumen
ustum.

1209. When alum is ignited with charcoal, a spontaneously inflammable compound results, which has long been known under the name of *Homborg's pyrophorus*. The potassa appears to be decomposed in this process, along with the acid of the alum, and pyrophorus is probably a compound of sulphur, charcoal, and potassium, with alumina.

Homborg's
Pyrophorus.

Pyrophorus may be prepared by the following process.

How prepar-
ed.

Mix equal parts of honey, or of brown sugar with powdered alum, in an iron ladle, melt the mixture over a fire, and keep it stirred till dry: reduce the dry mass to powder, add a few grains of potassa, and introduce it into a common phial coated with clay, and placed in a crucible of sand. Give the whole a red heat, and when a blue flame appears at the neck of the phial allow it to burn about five minutes, then remove it from the fire; stop the phial, and allow it to cool, taking care that air cannot enter it.

Dr Hare recommends the following method, which affords a pyrophorus that rarely fails.

Dr Hare's
process.

Take three parts of lamp-black, four of calcined alum, and eight of pearl-ashes; mix them thoroughly, and heat them in an iron tube to a bright cherry red for one hour. On removal from the fire the tube should be carefully stopped. When well prepared and poured out upon a glass plate, and especially when breathed upon, the pyrophorus kindles with a series of small explosions.† The inflammability of this compound arises from the presence of potassium.‡

* *First Princip.* i. 307.—Considerable differences exist in the statements which have been given by different analysts, of the composition of alum, as will appear from the following table:

| 100 parts contain | Acid. | Alumina. | Potassa. | Water. |
|------------------------------------|-------|----------|----------|----------|
| According to Vauquelin | 30,52 | 10,50 | 10,40 | 48,58 |
| — Dalton | 33, | 12, | 9, | 46, |
| — R. Phillips | 34,94 | 11,18 | 10,33 | 43,55 |
| — Berzelius | 34,23 | 10,86 | 9,81 | 46, |
| Do. corrected by Thomson | 33,82 | 10,86 | 9,90 | 45, |
| — Dr Thomson | 32,85 | 11,99 | 9,85 | 46,21 H. |

† The pyrophorus obtained by Dr Hare's process should be removed from the tube with great caution, as it has been found to explode violently on the introduction of a rod for the purpose of loosening it.—Silliman in *Amer. Jour. of Science*, x. 367.

‡ See *Alloys of Potassium*, p. 277.

Uses.

1210. Alum is of extensive use in the arts, more especially in dyeing and calico-printing, in consequence of the attraction which alumina has for the colouring matter.*

Neutral sulphate.

1211. A *neutral Sulphate of alumina* was obtained by Berzelius by the following process. He decomposed alum by ammonia; washed the precipitate, and re-dissolved it in sulphuric acid. To the liquor, after evaporation, he added alcohol, which threw down a sulphate nearly neutral, and rendered perfectly so, by being washed with farther portions. Gay-Lussac has also given the following process, for preparing a neutral sulphate of alumina.

Gay-Lussac's process.

On alum with base of ammonia, boil nitro-muriatic acid, till all the ammonia is destroyed, and evaporate to dryness to expel all the nitric and muriatic acids. The ammonia is decomposed by the chlorine, which results from the mutual action of those two acids, and the alumina remains in combination with sulphuric acid only. The saturated solution of this salt in water is an excellent test to discover potassa; for a drop or two, added to a solution of that alkali, or of any of its salts, immediately causes a precipitation of alum.† It is most probably constituted of 1 atom of acid + 1 atom of base. H. 1. 634.

SECTION X. Manganese.

Process for obtaining metallic manganese.

1212. The common ore of manganese is the black or peroxide, which is found native in great abundance. The metal is obtained by mixing this oxide, finely powdered, with pitch, making it into a ball, and putting this into a crucible, with powdered charcoal, one-tenth of an inch thick on the sides, and one-fourth of an inch deep at the bottom. The empty space is then to be filled with powdered charcoal, a cover is to be luted on, and the crucible exposed, for one hour, to the strongest heat that can be raised. Mr Faraday has succeeded in obtaining metallic manganese in large globules from the triple tartrate of manganese, by heating it in a crucible in a wind furnace *per se*. (H.) It is of a bluish white colour, very brittle, and difficult of fusion. When exposed to air it becomes an oxide. Its specific gravity is 8.013. It is not attracted by the magnet, except when contaminated with iron.

Oxides,

1213. *Manganese and Oxygen*.—There is a diversity of opinion among chemists as to the number of oxides of manganese, and their composition. According to Sir H. Davy

Soda alum.

* A triple sulphate of alumina and soda is described in the *Quarterly Journal of Science and the Arts*, (viii. 386.) in the form of irregular efflorescent octoëdra: it appears to contain 2 proportionals of sulphate of alumina, 1 proportional bi-sulphate of soda, and 28 proportionals water.

Ammoniacal Alum has been examined by Riffault (*Ann. de Chim. et Phys.* ix. 106) who found it to consist of 1 atom sulphate of ammonia, 3 atoms sulphate of alumina and 24 atoms water.

Magnesia, also, it appears, is capable of furnishing a base to alum; but it has not been applied to any useful purpose.

† *Ann. de Chim. et Phys.* vi. 201.

there are only two ;* Mr Brande admits three, Thenard four,† and Berezlius five.‡

It is certain, however, that there are three distinct oxides ; and it appears from the experiments of Thomson, whose results agree with those of Arfwedson§ and Berthier|| that they are thus constituted :—

| | Manganese. | | | Oxygen. | | |
|-----------------|------------|-----------|--|---------|-----------|--|
| Protoxide . . . | 28 | or 1 atom | | 8 | or 1 atom | |
| Deutoxide . . . | 28 | " " " | | 12 | " 1½ " | |
| Peroxide . . . | 28 | " " " | | 16 | " 2 atoms | |

Their composition.

1214. *Peroxide*.—This is the well known ore commonly called from its colour the black oxide, the nature of which was ascertained in 1774 by Scheele. It generally occurs massive, of an earthy appearance, and mixed with other substances, such as siliceous and aluminous earths, oxide of iron¶ and carbonate of lime. It also occurs crystallized with an imperfect metallic lustre. It may be made artificially by exposing the nitrate of manganese to a commencing red heat, until the whole of the nitric acid is expelled.

Peroxide.

1215. The peroxide of manganese undergoes no change on exposure to the air. It is insoluble in water, and does not unite either with acids or with alkalis. When boiled with sulphuric acid, it yields oxygen gas, and a sulphate of the protoxide is formed (287). With muriatic acid, a muriate of the protoxide is generated, and chlorine is evolved (301). On exposure to a red heat, it is converted with evolution of oxygen gas, into the deutoxide of manganese.

Properties.

1216. The peroxide of manganese is employed in the arts, in the manufacture of glass, and in preparing chlorine for bleaching. In the laboratory it is used for procuring chlorine and oxygen gases, and in the preparation of the salts of manganese.

Uses.

1217. The oxide of manganese which is sometimes called *black wad*, and which occurs in froth-like coatings on other minerals, is remarkable for its spontaneous inflammation with oil.—If half a pound of this be dried before a fire, and afterwards suffered to cool for about an hour, and it be then loosely mixed or kneaded with two ounces of linseed oil ; the whole, in something more than half an hour, becomes gradually hot, and at length bursts into flame. U. 573.

Black wad,

Spontaneous inflammation of.

1218. *Deutoxide of Manganese*.—This oxide combined with water sometimes occurs native. It is readily procured by exposing the peroxide of manganese to a low red heat ; and it is, therefore, the chief residue of the usual process for forming oxygen. By exposure to a white heat it is converted into what is called the red oxide of manganese.

Deutoxide.

* *Elements*, p. 369.

† *Traité de Chim.* ii. 331.

‡ For the results of several analyses, see Henry's *Chemistry*, vol. ii.

§ *Ann de Chim. et de Phys.* vi.

|| *Ibid*: xx.

¶ On the separation of iron from manganese, see *Quarterly Journal of Science and the Arts*, vol. vi. p. 153.

Properties.

1219. The deutoxide when reduced to powder is of a brown colour. On exposure to the air it slowly absorbs oxygen, and passes into the state of peroxide. It is dissolved by strong sulphuric and muriatic acids in the cold, forming deep red coloured solutions. With strong nitric acid it yields a soluble proto-nitrate, and an insoluble black powder which is the peroxide.*

Protoxide.

1220. *Protoxide of Manganese* is formed when a mixture of the deutoxide of manganese and charcoal is exposed to a strong red heat; or by passing a current of hydrogen gas over the deutoxide heated to redness in a tube of porcelain. This oxide is of a green colour when pure, but becomes brown on exposure to the air, owing to the absorption of oxygen. It is contained in all the salts of manganese, and, indeed, it is the only oxide of this metal which is capable of forming regular salts with acids.

Red oxide.

1221. The substance called the *red oxide* of manganese is formed by exposing the peroxide or deutoxide to a white heat, either in close or open vessels. It has a brownish red colour when in powder. Fused with borax or glass, it communicates to it a beautiful violet hue; concentrated hot nitric acid acts upon it in the same manner as on the deutoxide.

The red oxide contains more oxygen than the protoxide and less than the deutoxide. According to Arfwedson, it consists of 28 parts of manganese, and 10.4 parts of oxygen. It is probably a mixture or compound of the protoxide and deutoxide.

It has been inferred from some experiments of Berzelius and John, that there are two other oxides of manganese; which contain less oxygen than the green or protoxide.

Acids of manganese.

1222. Besides the oxides, manganese is capable of forming two acids with oxygen the *manganeseous* and the *manganesic acid*. When the peroxide of manganese is mixed with an equal weight of nitre or carbonate of potassa, and the mixture is exposed to a red heat, a green coloured fused mass is formed, which has been long known under the name of *mineral chameleon*. On putting this substance into water, a green solution is obtained, the colour of which soon passes into blue, purple and red; and ultimately, a brown flocculent matter, the deutoxide of manganese, subsides, and the liquid becomes colourless.

Mineral chameleon.

Exp.

Put equal quantities of this substance into two separate glass vessels, and pour on the one hot, and on the other cold water. The hot solution will have a beautiful green colour, and the cold one a deep purple. The same material, with water of different temperatures, assumes various shades of colour.

Theories.

1223. M. M. Chevillot and Edwards, have demonstrated that the peroxide of manganese, when fused with potassa, absorbs oxygen from the atmosphere, and is thereby converted into *manganesic acid*, which unites with the alkali. They

* Berthier.

attribute the different changes of colour above mentioned, to the combination of this acid with different proportions of potassa. By evaporating the red solution rapidly, they succeeded in obtaining a manganesiate of potassa in the form of small prismatic crystals of a purple colour. This salt yields oxygen to combustible substances with great facility, and detonates powerfully with phosphorus. It is decomposed when in solution by very slight causes, being converted into the deutoxide of manganese.

1224. The subsequent researches of Dr Forchhammer render it probable that the green and red colours are produced by two acids, the manganeseous and manganesic, the former giving rise to the green, and the latter to the red.

Dr Forchhammer infers that the first of the above acids contains three and the last four atoms of oxygen united with one atom of manganese.* T. 379.†

1225. *Manganese and Chlorine.*—By burning the metal in chlorine, or by exposing muriate of manganese to a strong heat, a pink semi-transparent flaky substance is obtained, which, when dissolved in water, produces a muriate of manganese. Manganese and Chlorine.

1226. M. Dumas has obtained a new chloride of manganese by putting a solution of manganesic acid into contact with sulphuric acid and fused common salt. Water and the new chloride are formed; the former is retained by the acid, the latter volatilizes in a gaseous form, with a greenish tint, and when passed into a tube cooled to 5° or 4° F., it condenses into a liquid of a brownish green colour. The most simple process appears to be to form a common green chameleon, to convert it into red chameleon by sulphuric acid, and to evaporate the solution, which will give a residue consisting of sulphate and manganesiate of potassa. This mixture acted upon by concentrated sulphuric acid produces the solution of manganesic acid, into which the common salt is to be thrown in small pieces until the vapours which rise are colourless; the latter effect is a sign that all the manganesic acid is decomposed, and that muriatic acid only is produced. This chloride of manganese corresponds in proportions to the manganesic acid; it is readily formed and examined, but not easily preserved. An analogous compound is obtained when a fluoride is used instead of the chloride.‡ M. Dumas' process.

1227. *Muriate of Manganese.*—The action of muriatic acid on the black oxide of manganese is most important. According to the old theory, part of the acid acts on one portion of the oxide; and first reduces it to the state of protoxide, and then dissolves it, affording muriate of protoxide of manganese. The oxygen thus liberated, uniting with another portion of Muriate.

* *Ann. of Philos.* xvi.

† According to an analysis of M. Unverdorben manganesic acid consists of
Manganese - - - - 58,74 Oxygen - - - - 41,26.

Ann. des Mines. 1827. 145.

‡ *Philos. Mag.* N. S. Feb. 1828.

muriatic acid, composes oxy-muriatic acid. But, on the more probable theory of chlorine, the hydrogen of the muriatic acid is attracted by the oxygen of the oxide, and the chlorine is not formed, but merely set at liberty.*

How obtain-
ed.

1228. Muriate of manganese is most easily formed by saturating muriatic acid with the carbonate. Heated in contact of air, it is decomposed, and oxide of manganese remains. The crystals of muriate of manganese consist of

Composition.

| | |
|----------------------------------|--------------------|
| Protoxide of Manganese | 1 atom |
| Muriatic acid | 1 " |
| Water | 4 atoms. H. 2. 10. |

Nitrate.

1229. *Nitrate of Manganese*.—Dilute nitric acid readily dissolves protoxide of manganese, and forms a very soluble and difficultly crystallizable *proto-nitrate*. The same salt may be obtained by digesting peroxide of manganese in nitric acid with a portion of gum or sugar, which abstracts oxygen, carbonic acid is evolved, and the protoxide dissolved by the acid. Exposed to light, the solution of the protonitrate lets fall a portion of peroxide of manganese.

When dilute nitric acid is poured upon the deutoxide of manganese, a protonitrate and peroxide are formed.

The composition of nitrate of manganese, according to Dr Thomson, is 1 atom acid 54, 1 protoxide 36, and 7 atoms water 63.†

Manganese
and Sulphur.

1230. *Manganese and Sulphur* appear unsusceptible of combination; but a compound of oxide of manganese and sulphur which is a bi-sulphuret is found in Transylvania and Cornwall. It is of a blackish grey colour, and metallic lustre. The *proto-sulphuret* may be obtained by igniting the sulphate with one-sixth of its weight of charcoal in powder.‡ It is also formed by the action of sulphuretted hydrogen on the proto-sulphate at a red heat.§ It dissolves completely in dilute sulphuric or muriatic acid, with disengagement of very pure sulphuretted hydrogen.|| T.

Sulphate.

1231. *Sulphate of Manganese* is formed by dissolving the protoxide or protocarbonate in the acid, and evaporating to

* According to Dr J. Davy the chloride consists of

| | | | |
|---------------------|-----|-----|--------|
| Chlorine | 54 | 100 | 117.64 |
| Manganese | 46 | 85 | 100 |
| | 100 | | |

Now 54 : 46 : : 30 : 30.6. The weight, therefore, of the atom of manganese, deduced from the chloride, exceeds that inferred from the oxide; but the discrepancy arises most probably from errors in analysis, and the true constitution of the chloride is

| | | | |
|---------------------|----|-----------|----|
| Manganese | 44 | or 1 atom | 28 |
| Chlorine | 56 | " 1 " | 36 |

Weight of its atom 64. H. 2. 8.

† *First Prin.* ii. 349.

‡ Berthier.

§ Arfwedson in *Ann. of Philos.* vii. N. S.

|| *Hyposulphite of Manganese* remains in solution when sulphate of manganese is decomposed by hyposulphate of lime.

dryness; a white *protosulphate* is formed, which crystallizes in rhomboidal prisms, and consists of

36 or 1 atom protoxide, 40 or 1 atom sulphuric acid, and 45 or 5 atoms water.

It is very soluble in water, and has a bitter styptic taste: at a bright red heat it gives out oxygen, and sulphurous acid and deutoxide of manganese remain. It may also be obtained by mixing peroxide of manganese into a paste with sulphuric acid, and heating it in a basin nearly to redness: oxygen is evolved, and the dry mass washed with water affords the sulphate.

1232. *Deutosulphate of Manganese* is formed by digesting the deutoxide in sulphuric acid diluted with its bulk of water: a red solution is formed, but the salt cannot be obtained in a neutral or separate state, for the application of heat evolves oxygen, and forms protosulphate. It is, probably, to a little deutosulphate that the occasional red tinge of the protosulphate is to be attributed. Deutosulphate.

1233. *Carbonate of Manganese* is white, insipid, and insoluble in water. It is precipitated by alkaline carbonates from the protomuriate or protosulphate, and consists of 1 atom protoxide, 1 atom carbonic acid, and 1 water. Carbonate.

1234. The salts of manganese containing the protoxide are mostly soluble in water, and the solution becomes turbid and brown by exposure to air. They are not precipitated by hydriodic acid; they furnish white precipitates with the alkalies, which soon become discoloured by exposure to air; they are precipitated white by ferro-cyanate of potassa, and yellow by hydrosulphuret of ammonia. Characteristics of the proto-salts of manganese.

1235. The native peroxide of manganese is used in the laboratory as a source of oxygen, and is largely employed in the preparation of chlorine, especially by the bleachers. It is used in glass-making, and, when added in excess, gives it a red or violet colour. It is also employed in porcelain painting; and it gives common earthen ware a black colour, by being mixed with the materials before they are formed into vessels. Usés.

SECTION XI. *Iron.*

1236. The most important native combinations of iron, whence the immense supplies for the arts of life are drawn, are the oxides. Iron is also found combined with sulphur, and with several acids; it is so abundant that there are few fossils free from it. It is also found in some animal and vegetable bodies, and in several mineral waters.

Iron is a metal of a blue white colour, fusible at a white heat. Its specific gravity is 7.78. It has not been so long known as many of the other metals; it was, however, employed in the time of Moses for cutting instruments. It is extremely ductile, but cannot be hammered out into very thin leaves. Properties.

Native.

1237. Iron is sometimes found native, and is usually regarded as of meteoric origin, for it is invariably alloyed by a portion of the metal nickel, and a similar alloy is found in *meteoric stones*. *Native Iron* is flexible, cellular, and often contains a green substance of a vitreous appearance. It has been found in Africa, in America, and in Siberia, where a mass of it weighing 1600 lbs was discovered by Professor Pallas. The mass found in Peru, described by Don Rubin de Celis, weighed 15 tons.*

Combines with oxygen.

1238. *Iron and Oxygen*.—Exposed to heat and air iron quickly oxidizes, or in common language, rusts. If the temperature of the metal be raised, this change goes on more rapidly, and when made intensely hot, takes place with the appearance of actual combustion. Thus the small fragments, which fly from a bar of iron during forging, undergo a vivid combustion in the atmosphere; and iron filings, projected upon the blaze of a torch, burn with considerable brilliancy. The oxide, obtained in these ways is of a black colour, and is still attracted by the magnet.

Effect of water, at common temperatures.

1239. By contact with water at the temperature of the atmosphere, iron becomes slowly oxidized, and hydrogen gas is evolved. It has been contended by Dr Marshall Hall,† that water, provided it be entirely deprived of oxygen gas, and secured from contact with atmospheric air, does not oxidate iron at common temperatures; but it has been shown by M. Guibourt,‡ that this inaction of pure water on iron, takes place only when the quantity of metal relatively to the fluid is very small; and that a temperature of from 120° to 140° F. renders water decomposable by iron, especially when the metal bears a considerable proportion to the water.

Of steam.

1240. When the steam of water is brought into contact with red-hot iron, the iron is converted into the black oxide; and an immense quantity of hydrogen gas is set at liberty (391). The iron is found to have lost all its tenacity, and may be crumbled down into a black powder, to which the name of *finery cinder* was given by Dr Priestly. In composition it does not appear to differ from the oxide of iron obtained by the action of atmospheric air, and it is strongly magnetic. By a careful repetition of the process, Dr Thomson found, that 100 grains of iron, ignited in contact with the vapour of water, acquire 29,1 grains of oxygen.

Of dilute sulphuric acid.

1241. When iron is dissolved in diluted sulphuric acid, the acid is not decomposed; but the metal is oxidized at the expense of the water, and hydrogen gas is obtained in abundance. (371). Now as water is composed of two volumes of hydrogen and one of oxygen, a quantity of oxygen, equal in volume to half the hydrogen gas obtained, must have combined with the metal; that is, for every 200 cubic inches of hydrogen, oxygen equal

* Many masses are scattered over the continent of North America, for which see Cleaveland's *Mineralogy*, 583.

† *Jour. Roy. Inst.* vii. 55.

‡ *Ann. de Chim. et Phys.* xi. 40.

to 100 cubic inches or 33,8 grains must have united with the metal. But 100 grs. of pure iron evolve by acting on dilute sulphuric acid 170 cubic inches of hydrogen gas at a mean of the barometer and thermometer, showing that oxygen = 85 cubic inches, or 28,73 grs. must have united with the metal, during its solution. Dr Thomsom, from an experiment of this kind, found that 35 grains of iron, after the action of dilute sulphuric acid, had gained 10 grs. of oxygen, 59 cubic inches of hydrogen being evolved. It is to be considered, however, that the purity of the iron employed will materially affect the result; for if the iron contain charcoal, as is almost always the case, carburetted hydrogen will be mixed with the hydrogen; and the hydrogen in this gas being in a condensed state, the apparent will be less than the real quantity of hydrogen disengaged.

Iron, by the last process which has been described, is converted into an oxide of a black colour, still retaining the magnetic property. H. 2. 22.

1242. The *protoxide of iron* may be procured by precipitating a solution of sulphate of iron by potassa, washing the precipitate out of the contact of air, and drying it at a red heat. It is black, and consists of 28 iron + 8 oxygen = 36. Protoxide!

The recently precipitated protoxide of iron is sparingly soluble in ammonia, and in carbonated alkalies.

Protoxide of iron may also be obtained by burning iron in oxygen gas; this very beautiful experiment was devised by Dr Ingenhouz, and is best performed by attaching a straight piece of watch spring, wound round with harpsichord wire, to the stopper of an air-jar of oxygen gas: as the wire burns, it drops in black globules of oxide into the water beneath. Pl. iii. fig. 78.

This oxide of iron used to be prepared for pharmaceutical use, by moistening iron filings with a small quantity of water, and exposing them to the air for a day or two; a quantity of black oxide thus forms, which is separated by washing, and the process repeated till the whole of the metal is thus oxidized. It was called *martial ethiops*. It is black, tasteless, and insoluble in water.

1243. When protoxide of iron is boiled in nitric acid, and precipitated by ammonia, washed, and dried at a low red heat, it increases in weight and acquires a brown colour. This is the *peroxide** composed of 28 iron + 12 oxygen = 40. It may be also obtained by igniting green vitriol, and was formerly known by the name of *crocus martis*, or *Saffron of Mars*, and *colcothar*. Crocus martis.

M. Gay-Lussac† has detailed some experiments, which he considers as demonstrating the existence of a third definite oxide of iron, intermediate between the above oxides, and

* *Tritoxide* of Thenard, ii. 341, edit. 4.

† *Ann. de Chim. et Phys.* i. and *Ann. de Chim.* lxxx.

composed of iron 100 + oxygen 37,8. It is probably a compound of 1 atom of the protoxide and 2 atoms of peroxide. H.

Equivalent
number.

In order that the representative number of iron may also be its equivalent number, it is represented by 28. But the peroxide, instead of consisting of 1 proportional metal + 2 oxygen, consists of 1 proportional metal + 1,5 oxygen; and the chloride and perchloride bear the same relation to each other. The case however is different with the sulphurets; for the sulphuret consists of 1 proportional iron + 1 sulphur: and the bi-sulphuret of 1 iron + 2 sulphur.

M. Gay-Lussac has shown the curious fact, that although red-hot iron decomposes water, hydrogen is capable of decomposing all the oxides of iron at a red heat.*†

Native
Oxides.

1244. The *Native Oxides of Iron* constitute a very extensive and important class of metallic ores. They vary in colour, depending upon mere texture in some cases; in others, upon the degree of oxidizement. Some varieties are magnetic, and those which contain least oxygen are attracted by the magnet. The most important are *Magnetic Iron Ore*, which occurs massive, and crystallized in octoëdra. Its specific gravity is 4,5. It is often sufficiently magnetic to take up a needle. It occurs chiefly in primitive countries, and is very abundant in Sweden, where it is manufactured into a bar-iron particularly esteemed for making steel.

Iron glance.

Another variety of oxide of iron is called *iron glance*, and *micaceous iron ore*. It is found in the isle of Elba; and among volcanic products. A third variety is *Hæmatite*, or red iron-stone; it occurs in globular and stalactitic masses, having a fibrous and diverging structure. Most of the British iron-plate, and wire, is made from it.

A fourth variety of oxide of iron is known under the term of *clay iron-stone*, on account of the quantity of argillaceous earth with which it is contaminated. Though this is far from the purest iron ore found in Great Britain, it is the chief source of the cast and bar-iron, in ordinary use. Its employment is chiefly referable to the coal which accompanies it.

Reduction of
iron ores.

The essential part of the process by which these ores of iron are reduced, consists in decomposing them by the action of char-

* *Ann. de Chim. et Phys.* i. 37.

† According to Stromeyer, when hydrogen gas is conducted over peroxide of iron, at temperatures below that at which complete reduction is effected, a partial deoxidation ensues, and the peroxide is converted into a real protoxide of iron. This oxide has a dark blackish blue colour, appearing almost black by reflected light. It stains glass blue, and is the cause of that colour in iron slag. It is highly combustible, and if after its formation it be protected from the air by an atmosphere of hydrogen till quite cold, it will take fire the instant it is placed on a saucer, so as to be exposed to the air, but, instead of passing like metallic iron into the black oxide, it is completely converted into peroxide. M. Stromeyer refers the ignition of metallic iron, to the presence of this protoxide, and states that, when thoroughly reduced by hydrogen, the pure iron will not inflame at temperatures below the fusing point of cadmium. M. Stromeyer contends for the existence of only two oxides of iron, the blue and the red. M. Magnus, contends that it is the iron which inflames, and not a protoxide, and that oxide of iron is completely reduced by hydrogen at a temperature between the boiling point of mercury and fusing point of zinc.—*Brewster's Jour.* v. 301.

coal at high temperatures. The argillaceous iron of Wales, Shropshire, &c. is first roasted, and then smelted with lime-stone and coke: the use of the former being to produce a fusible compound with the clay of the ore, by which the latter is enabled to act upon the oxide, and to reduce it to the metallic state.

1245. The two oxides of iron form distinct salts with the acids.

The salts containing the protoxide are of a green colour, mostly crystallizable, become reddish brown by exposure to air, and their solutions absorb nitric oxide gas and become of a deep olive colour. The salts with the per-oxide do not, with very few exceptions, crystallize: they are brown, soluble in alcohol, and do not absorb nitric oxide. Salts of iron.

The alkalis precipitate hydrated oxides from these solutions.

1246. *Iron and Chlorine* unite in two proportions; the *Proto-chloride* may be obtained by evaporating *protomuriate of iron* to dryness, and exposing the residuum to a red heat, out of the contact of air. A grey, brittle, lamellar substance is formed, which consists of 1 atom of each element. Chloride.

1247. When iron wire is heated in chlorine, it burns with a red light, and produces a compound which rises in beautiful brown scales. It is the *perchloride of iron*. It consists of Composition.

| | | | | | | |
|----------|-----------|------|-----------|------|-----------|---------|
| Chlorine | . . . | 66,1 | | 100 | | 194,174 |
| Iron | | 33,9 | | 51,5 | | 100. |
| <hr/> | | | | | | |
| 100. | | | | | | |

In this case we have also the apparent anomaly of an atom and a half of chlorine being united with an atom of iron, for $100 : 51,5 :: 36 \times 1\frac{1}{2} = 54,28$. H. 2. 22. This, and similar anomalies, are best reconciled, Dr Henry conceives, by multiplying by 2 the numbers expressing the proportions, which will make the ratio as 2 to 3, instead of as 1 to $1\frac{1}{2}$.^{*} The chloride and perchloride of iron produce *protomuriate*, and *permuriate* of iron when acted upon by water. Perchloride.

1248. *Iron and Iodine* unite and form a brown fusible compound which decomposes water, and is converted into the hydriodate. Iron and Iodine.

1249. *Muriate of Iron*.—Muriatic acid dissolves iron and its oxides with great ease; and affords two distinct salts, differing from each other according to the state of oxidation of the metal. The muriate containing the black, or protoxide, is green, and that containing the oxide at the maximum, or peroxide, red. Murietes.

^{*} That the chlorine in the protochloride of iron is to that in the perchloride as 1 to 1,5, is shown by Dr Davy in his valuable paper on the chlorides, (*Phil. Trans.* 1812, 169.) and the equivalent number of iron, as deduced from his analysis is somewhat above 28. It must be confessed that the anomaly in the oxides and chlorides of iron throws some difficulty in the way of applying to them their equivalent numbers, but as the foundations of chemistry are purely experimental, we must not endeavour to do away that difficulty by a theoretical substitute. There is a difference in the relations of iron to oxygen and chlorine, compared with its relations to sulphur, which does not exist elsewhere; of the cause of this difference we are at present ignorant. D.

Protomuri-
ate.

1250. The green or *protomuriate of Iron* is best obtained by digesting black sulphuret of iron in dilute muriatic acid; sulphuretted hydrogen is evolved, and a green solution obtained, which, filtered and evaporated, yields pale green crystals, very soluble, and of a styptic taste. This salt abundantly absorbs nitric-oxide gas; the solution is of a very deep brown colour; when heated, red oxide of iron falls and a portion of ammonia is formed; a great part of the gas at the same time escapes.

This salt may also be obtained by dissolving iron filings in muriatic acid excluded from air; but the above process is preferable, as the sulphuretted hydrogen prevents any part of the iron passing into the state of permuriate.

Permuriate.

1251. *Permuriate of Iron* is formed by digesting the peroxide in muriatic acid: it dissolves without the evolution of chlorine, and when evaporated to dryness, furnishes a reddish brown deliquescent mass of a very astringent taste, soluble both in water and alcohol. It forms the basis of the *tinctoria muriatis ferri* of the *Pharmacopœia*. Permuriate of iron is also formed by exposing the protomuriate to air.

Berzelius describes a striking experiment founded on this property.

Exp.

If a solution of the green muriate be exposed to the atmosphere, in a tall cylindrical glass jar, for some days, and a few drops of pure ammonia be then introduced at different depths, by means of a tube, the precipitate formed near the surface will be green, a little lower blue; still lower greyish; then of a dirty white; and at the bottom perfectly white, provided time has not been allowed for the atmospheric oxygen to penetrate so low. H. 2. 29.

Effect of
heat.

1252. When permuriate of iron is exposed to heat, muriatic acid, chlorine, and water are evolved, chloride of iron sublimes, and a portion of peroxide remains in the retort.

1253. When muriate of ammonia and peroxide of iron are mixed and exposed to heat in a proper subliming vessel, a yellow sublimate is obtained, which is the *ens veneris* and *flores martiales* of old pharmacy; the *ammoniae et ferri murias* of the *Pharmacopœia*; it consists chiefly of muriate of ammonia, with a small but variable proportion of permuriate of iron.

Nitrate.

1254. *Nitrate of Iron*.—The nitrate of iron, it was long ago shown by Sir H. Davy, may exist in two different states, the green or proto-nitrate, in which the oxide is at the minimum of oxidation, and the red, in which it is at the maximum.

Method of
obtaining in
the large
way.

To obtain nitrate of iron, in which the oxide is at the minimum, acid of the specific gravity of 1.25, or even less, must be used; the iron must be added in large pieces, and at distant intervals, and the operation carried on without the access of air. When this solution is made on a large scale for the purposes of the dyer, it is proper to connect the vessel in which it is prepared, with a large receiver; for in the latter, a quantity of nitrous acid will be found, which is worth the trouble of collecting. H. 2. 28.

1255. Nitrate of iron thus prepared, passes, on exposure to the atmosphere, to the state of that in which the oxide is at the

maximum; or we may obtain the per-nitrate by leaving nitric acid for a long time in contact with protoxide of iron. Crystals form spontaneously in the liquid, which are at first transparent and colourless, but become brown by keeping; their taste is acid and astringent, and they redden vegetable blues. They contain per cent. 18 base, 41 acid, and 41 water. H. 2. 28.

1256. *Sulphur and Iron*.—Iron combines with sulphur, and affords compounds, the characters of which vary greatly according to the proportions of their components. (a) A paste of iron filings, sulphur and water, if in sufficient quantity, will burst, after some time, into a flame. (b) A mixture of one part of iron filings and three parts of sulphur, accurately mixed, and melted in a glass tube, at the moment of union, exhibits a brilliant combustion. The best method, however, of effecting the combination of iron and sulphur is to take a bar of the metal, while of a glowing heat, from a smith's forge, and to rub it with a roll of sulphur.* The compound of iron and sulphur falls down in drops, and may be preserved in a phial. Of the compounds of sulphur, this is one of those which are best adapted for affording pure sulphuretted hydrogen gas with diluted acids. (c) Berthier formed the proto-sulphuret of iron by heating the proto-sulphate in a charcoal crucible. Sulphuret.

In the sulphuret, made artificially by fusion, as well as in the native sulphuret, iron (it has been shown by Proust and Mr Hatchett) is in the metallic state. Two compounds of iron and sulphur have been proved to exist, the one with a smaller, the other with a larger proportion of sulphur. The former, which is distinguished by the property of being magnetic, is the *proto-sulphuret*. The *bi-sulphuret* is known only as a natural product; it is not magnetic, is nearly insoluble in diluted sulphuric and muriatic acids; and gives no sulphuretted hydrogen gas with acids. But the proto-sulphuret is readily soluble in dilute acids, and gives during solution abundance of sulphuretted hydrogen. It is composed of 28 iron + 16 sulphur; and the yellow, or bi-sulphuret, of 28 iron + 32 sulphur. H. 2. 35.

1257. The natural sulphurets of iron are called *iron pyrites*, Iron pyrites. and Mr Hatchett has shown that the *magnetic pyrites* contains just half the proportion of sulphur existing in the *common pyrites*.†

The principal use of pyrites is in the formation of *green vitriol*, for which purpose the ore is gently roasted and exposed to air and moisture. Some varieties are spontaneously decomposed, and furnish this salt. Pyrites has also lately been used in the production of sulphuric acid. Use.

1258. *Sulphate of Iron*.—When diluted sulphuric acid is made to act upon iron, we obtain a compound of that acid with the protoxide, a *protosulphate of iron*. The solution yields crystals, which have a beautiful green colour, and the shape Sulphate.

* See *Amer. Jour. of Science*, viii. 104.

† *Phil. Trans.* 1804.

of oblique rhombic prisms, not of rhomboids, as is sometimes represented.* They have a styptic taste, and are soluble in about 2 of cold parts and $\frac{3}{4}$ ths their weight of boiling water, but insoluble in alcohol.

Copperas.

1259. This salt is called *copperas* or *green vitriol*, and is often prepared by exposing roasted pyrites to moisture, in which case it is impure. It is usually formed by dissolving iron filings, or turnings, in dilute sulphuric acid, filtering and evaporating the solution, and setting it aside to crystallize. It is also obtained, perfectly free from persulphate, by acting upon sulphuret of iron by dilute sulphuric acid. It consists of one proportional of protoxide = $36 + 1$ proportional of acid = 40, and in its crystallized state contains seven proportionals of water = 63. Its solution absorbs nitric oxide gas, and acquires a deep brown colour; it also absorbs chlorine, muriatic acid is formed, and the iron becomes peroxidized so that water is here decomposed.

Absorbs oxygen by exposure to air.

1260. Exposed to air and moisture, the protosulphate of iron gradually absorbs oxygen, and is partly converted into a persulphate.† It may also be converted into persulphate by nitric acid. When heated, it fuses in its water of crystallization, and at a high temperature evolves a mixture of sulphurous and sulphuric acids, peroxide of iron remaining in the vessel: by this process sulphuric acid used formerly to be prepared, and the residue was known under the name of *caput mortuum vitrioli* or *colcothar*. If the green crystals of this salt be exposed to a temperature of about 300° , they lose a portion of water, and crumble down into a white powder.‡

Persulphate.

1261. *Persulphate of Iron* is obtained by dissolving the moist red oxide in dilute sulphuric acid; it does not crystallize, but affords, by evaporation, a brown deliquescent mass, consisting of 1 proportional of peroxide + 1,5 sulphuric acid, or 40 oxide + 60 sulphuric acid. It is formed in the mother waters of the sulphate. Its taste is highly astringent, and when dry it becomes white.

* *Ann. of Philos.* xi. 264.

† When a solution of proto-sulphate of iron is heated with access of air, part of the protoxide passes to the state of peroxide, and combining with a portion of acid, falls down in the form of a yellow powder, which, according to Berzelius, is a sulphate of the peroxide with *excess of base*, or a *sub-persulphate*. The proportions of its components are

| | | Atoms. | |
|------------------|------------|-----------|-------|
| Sulphuric acid | - - - 15,5 | - 1 - - - | = 40 |
| Peroxide of iron | - - - 63, | - 4 - - - | = 160 |
| Water | - - - 21,5 | - 6 - - - | = 54 |
| | 100, | | 254 |

Other sulphates with base of peroxide of iron (called from the atomic proportions of their constituents *per-bisulphate*, and *per-quadrissulphate*), have been investigated by Dr Thomson and others. (*Ann. Philos.* x. 102. xiii. 466 and 298.); but no sulphate of protoxide with *excess of acid* is yet known. The sulphurous acid, also unites with protoxide of iron, and forms a *sulphite*; and this sulphite, taking an additional quantity of sulphur, composes a *sulphuretted sulphite*. H. 2. 27.

Native.

† *Native Green Vitriol* is frequently found associated with iron pyrites, being produced by its decomposition: it occurs in some coal mines.

1262. *Phosphuret of Iron* may be formed by dropping phosphorus into a crucible containing red-hot iron wire; it is a brittle grey compound, and acts upon the magnet.* Phosphuret.

1263. *Phosphates of Iron*.—These are both insoluble, and may be formed by adding solution of phosphate of soda, to protosulphate and persulphate of iron. The *protophosphate* of iron is of a pale blue colour; the *perphosphate* is white. Phosphates.

1264. *Native Protophosphate of Iron* occurs in the form of a blue earthy powder, and also in prismatic crystals.† The former has sometimes improperly been termed *Native Prussian Blue*, and has been found in alluvial soil: the latter occurs with iron pyrites in Cornwall. Native.

1265. *Iron and Carbon*.—Iron combines with carbon in various proportions; and the varieties of proportion occasion great differences of properties in the compounds. On these varieties, and the occasional combination of a small proportion of oxygen, depend the qualities of the different kinds of iron used in the arts, as cast-iron, steel, &c. &c. Carburet.

1266. The substance termed *Plumbago*, *Graphite*, or *Black Lead*, is generally regarded as a true *carburet of iron*: this is not an uncommon mineral, though rarely found of sufficient purity for the manufacture of pencils:‡ the coarser kinds and the dust, are melted with sulphur to form common carpenters' pencils: crucibles are sometimes made of it, and it forms an ingredient in compositions for covering cast-iron, and for diminishing friction in machines. According to Messrs Allen and Pepys it consists of Plumbago.

$$95 \text{ carbon} + 5 \text{ iron} = 100.$$

Plumbago burns with great difficulty: its composition was ascertained by the above-mentioned chemists, by exposing it in the apparatus used for burning the diamond, to a current of oxygen at a red heat, and ascertaining the quantity of carbonic acid and of oxide of iron thus produced.§ When intensely heated in a Toricellian vacuum by a Voltaic battery, Sir H. Davy found that its characters remained wholly unaltered, neither could any evidence of its containing oxygen be derived from the action of potassium. But when exposed to the focus of a powerful burning lens in oxygen gas, it was observed that the gas became clouded, and that dew was deposited, indicating the presence of hydrogen or of water.|| Effect of heat, &c.

1267. *Carbonate of Iron*.—The only oxide of iron, so far as is yet known, that is capable of uniting with carbonic acid, Carbonate.

* Upon the subject of the magnetic qualities of the sulphuret and phosphuret of iron, the reader is referred to Mr Hatchett's analysis of the magnetic pyrites.—*Phil. Trans.* 1804.

† See Cleaveland's *Mineralogy*, 618.

‡ See a description of the mine at Borrodale. *Boston Jour. of Philos.* ii. 332.

§ An ingenious mode of analysis employed by Mr Mushet, consists in ascertaining the quantity of litharge which a given quantity of the iron under examination is capable of reducing to a metallic state.

|| On the fusion of plumbago by means of Dr Hare's Deflagrator, see *Amer. Jour.* vi. 344, &c.

is the protoxide. Proto-carbonate of iron is found native, consisting of 1 atom of protoxide + 1 atom of carbonic acid. It has not been formed artificially; nor are we acquainted with any solid compound of the peroxide of iron with carbonic acid. The *sub-carbonate* of the London Pharmacopœia* is composed of about 40 per cent. carbonate of iron, and 60 of the peroxide.†

Ferro-cyanate or Prussian Blue.

1268. *Ferro-cyanate of Iron* or *Prussian Blue* is usually prepared by the following process:—Equal parts of subcarbonate of potassa and some animal substance, such as dried blood, or horn shavings, are heated red hot, in a crucible, and six or eight parts of water are poured upon the mixture when it has quite cooled. The solution is filtered, and found to contain *cyanide of potassium*. It is mixed with a solution containing two parts of alum and one of proto-sulphate of iron; a precipitate falls, at first of a dingy green hue, but which, by copious washings with very dilute muriatic acid, acquires a fine blue tint, and is called *Prussian Blue*, having been discovered by Diesbach, a colour-maker of Berlin, in 1710. The first description of the mode of preparing it is given by Woodward in the *Phil. Trans.* for 1724.

Theory.

1269. In this process the animal matter is decomposed, and resolved into a variety of products arising from the reunion of its ultimate component parts. The matter remaining in the crucible contains cyanide of potassium, and when acted upon by water, hydrocyanate of potassa, with a little carbonic acid and ammonia, is formed in consequence of the decomposition of a portion of the water; and consequently the principal salts contained in the washings of the black matter remaining in the crucible are carbonate and hydrocyanate of potassa, which, when added to a solution of sulphate of iron, form a precipitate of oxide and ferrocyanate of iron; the former is removed by the dilute muriatic acid. The aluminous earth of the alum gives a *body* to the precipitate, which improves it as a pigment.

The above seems to be the simplest view of the formation and composition of Prussian blue; a variety of other opinions respecting its nature have been entertained, but they require further experimental verification. B.

Method of preparing it for chemical purposes.

1270. The prussian blue of commerce is an impure substance, and contains a variety of other matters, especially a quantity of alumina. For chemical experiments, it is proper, therefore, to prepare it by mixing the solutions of ferrocyanate of potassa and proto-sulphate or proto-muriate of iron, and washing the precipitate, first with muriatic acid, and then with water. The precipitate produced is at first an exceedingly light blue, and continues so, as long as it is guarded from the action of the atmosphere; but it changes to a deeper blue by exposure to the air, or by mixture with any agent capable of imparting oxygen. If per-sulphate of iron be substituted for the proto-

* *Ferri Carbonas*, U. S. P.

† Phillips.

sulphate, the precipitate is at first apparently of a fine colour, but becomes by drying almost black.

1271. Prussian blue is insoluble in water, and in acids, unless Properties. when they are concentrated and heated. When thoroughly dried, it shows a great affinity for moisture, by absorbing it rapidly from the atmosphere. It is not decomposed by being heated to 307° F.; but, at a higher temperature, it catches fire and burns in the manner of tinder, leaving from 54 to 60 per cent. of oxide of iron.

Prussian blue submitted to distillation *per se* gives water, hydrocyanate of ammonia, carbonic acid, and other gases.* H. 2, 31.

1272. The salts of iron are mostly soluble in water and the solution is reddish brown, or becomes so by exposure to air. It affords a blue precipitate with ferrocyanate of potassa; and a black precipitate with hydrosulphuret of ammonia. Infusion of gall-nuts produces a black or deep purple precipitate. The hydriodic acid occasions no change. Characters of salts of iron.

1273. Of the *alloys* of iron, *tin-plate* is that most used. Alloys. It is made by dipping clean iron plates into melted tin. The process is described at length by Mr Parkes.† When tin-plate is washed over with a weak acid, the crystalline texture of the tin becomes beautifully evident, forming an appearance which has been called *moiré metallique*.‡

1274. An extremely important part of the chemical history of iron relates to the varieties of the metal which are found in commerce. These are much too numerous to be dwelt upon here; so that we shall limit our observations to the principal of them only, which are *cast iron*, *wrought iron* and *steel*.

Of cast iron there are two principal varieties, distinguished Cast iron. by the terms *white* and *grey*. The first is very hard and brittle, and when broken, of a radiated texture. Acids act upon it but slowly, and exhibit a texture composed of a congeries of plates, aggregated in various positions.§

Grey or mottled iron is softer and less brittle; it may be bored, and turned in the lathe. When immersed in dilute muriatic acid, it affords a large quantity of black insoluble matter, which Mr Daniell considers as a triple compound of carbon, iron, and silicon, and which has some very singular properties. The texture of the metal resembles bundles of minute needles. Grey iron.

1275. Cast iron is converted into wrought iron by a curious process, called *puddling*. Process of puddling. The cast iron is put into a reverberatory furnace, and when in fusion is stirred, so that every part

* Besides Prussian blue, there appears from Berzelius' experiments (*Ann. of Philos.* N S. i. 444.) to be another blue compound of the same elements, which is soluble to some extent in water. Prussian blue, in the dingy green state in which it is first precipitated seems also to contain an excess of base, which muriatic acid removes. There are probably, therefore, three compounds in which the peroxide, and one in which the protoxide, exists as base. H.

† *Boston Jour. of Philos.* ii. 243.

‡ *Quarterly Jour. of Science*, vol. v. 368.

§ Daniell, *Quart. Jour. Sci. and Arts.* vol. ii. 220.

may be exposed to the air and flame. After a time the mass heaves, emits a blue flame, and gradually grows tough and becomes less fusible, and at length congeals. In that state it is passed successively between rollers, by which a large quantity of extraneous matter is squeezed out, and the bars are now malleable. They are cut into pieces, placed in parcels in a very hot reverberatory furnace, and again hammered and rolled out into bars. They are thus rendered more tough, flexible and malleable, but much less fusible, and may be considered as nearly pure iron.

Analysis shows that cast iron contains oxygen, carbon, often sulphur and phosphorus, either silica or silicon, and it appears very probable that calcium exists in some of the varieties.

By the process of puddling and rolling, these substances are burned away or squeezed out, and thus malleability is conferred upon the metal by rendering it more pure. A specimen of cast iron analyzed by Berzelius afforded iron 91,53—manganese 4,57—carbon 3,90.

Structure of wrought iron.

A bar of wrought iron, when its texture is examined in the mode pointed out by Mr Daniell, presents a fasciculated appearance, the fibres running in a parallel and unbroken course throughout its length. This structure may be well seen by tearing a bar of wrought iron asunder.

Steel.

1276. *Steel* is a compound of iron with carbon, the proportions being variable. It combines the fusibility of cast with the malleability of bar iron, and when heated and suddenly cooled it becomes very hard, whence its superiority for the manufacture of cutting instruments. If kept for a long time in fusion, it loses carbon and becomes pure iron.

Cementation.

Iron is converted into steel by a process called *cementation*, which consists in heating bars of the purest iron in contact with charcoal: It absorbs carbon and increases in weight, at the same time acquiring a *blistered* surface. This, when drawn down into smaller bars and beaten, forms *tilted steel*; and this broken up, heated, welded, and again drawn out into bars, forms *shear steel*. *English cast steel* is prepared by fusing blistered steel with a flux composed of carbonaceous and vitrifiable ingredients, casting it into ingots, and afterwards, by gentle heating and carefully hammering, giving it the form of bars.*

1277. Messrs Stodart and Faraday found, that by intensely heating pure steel with charcoal powder, a *carburet of iron*, of a dark grey colour, very brittle and highly crystalline was formed, which afforded upon analysis

$$94,36 \text{ iron} + 5,64 \text{ carbon} = 100.$$

In this compound, which was frequently made and afforded the same results on analysis, and which therefore may be re-

* Mr Dalton conceives that the properties which distinguish steel from iron are rather owing to a peculiar crystallization or arrangement of the ultimate particles of iron, than to their combination with carbon or any other substance. *New System*, &c. vol. 2d. p. 216.

garded as definite, the proportion of carbon very far exceeds that in steel, so that the latter is probably a compound of pure iron with a variable proportion of the true carburet.*

1278. *Wootz* or *Indian steel* is truly valuable for the purpose of making edge tools. Its peculiar excellence is owing to combination with a minute portion of the earths alumina and silica: or rather, perhaps, with the bases of these earths.† Whether the earths are found in the ore, or are furnished by the crucible used in making the steel, is not certainly known; nor is the Indian steel-maker probably aware of their presence. *Wootz*, in the state in which it is imported, is not fit to make into fine cutlery. It requires a second fusion, by which the whole mass is purified and equalized, and fitted for forming the finest edge instruments. Wootz.

1279. When steel is heated to a cherry-red colour, and then plunged into cold water, it becomes so extremely hard and brittle, as to be unfit for almost any practical purpose. To reduce it from this extreme hardness, is called by the workmen *tempering*, and is effected by again heating the steel to a certain point. The surface being a little brightened exhibits, when heated, various colours which constantly change as the temperature is increased, and by these colours it has been customary to judge of the temper of the steel. Tempering.

A more accurate as well as convenient method is to use a bath and thermometer; the bath may be of mercury, or of the fusible mixture of lead, tin, and bismuth, or, indeed, of any fluid whose boiling point is not much under 600°. Into this bath the articles to be tempered are put, together with the bulb of a thermometer graduated to near the boiling point of mercury. The corresponding degrees at which the various colours appear, are from 430° to 600°. The first change is at about 430°, but this is too faint to be distinguished, except by comparison with another piece of untempered polished steel. At 460° the colour is straw, becoming deeper as the temperature is increased; at 500° the colour is brown; this is followed by a red tinge with streaks of purple, then purple, and at nearly 600° it is blue.

* The following table, drawn up by Mr Mushet, shows the quantities of charcoal which disappeared during the conversion of iron into the different *subcarburets of iron* known in commerce.—*Phil. Mag.* xiii.

| Charcoal absorbed, | RESULTS. |
|---------------------------|---------------------------------|
| $\frac{1}{120}$ - - - - - | soft cast steel, |
| $\frac{1}{100}$ - - - - - | common cast steel, |
| $\frac{1}{90}$ - - - - - | the same, but harder, |
| $\frac{1}{50}$ - - - - - | the same: too hard for drawing, |
| $\frac{2}{5}$ - - - - - | white cast iron, |
| $\frac{2}{0}$ - - - - - | mottled cast iron, |
| $\frac{1}{50}$ - - - - - | black cast iron. |

When the carbon amounts to $\frac{1}{60}$ of the whole mass, the hardness is at a maximum.

† *Quarterly Journal of Science*, vii. 288.

The degrees at which the respective colours are produced being thus known, it follows that the workman has only to heat the bath, with its contents up to the required point. For example, suppose the blade of a penknife (or one hundred of them) to require tempering: they are suffered to remain in the bath until the mercury in the thermometer rises to 460° , and no longer, that being the heat at which the knife (supposing it to be made of the best English cast steel) will be sufficiently tempered.

The advantages attending this method are obvious: the heat is equally applied to the whole; and the workman, instead of attending to the colour of each blade, has only to observe the thermometer.

1280. Some recent experiments, proving that steel, for certain uses, is sufficiently tempered long before it is heated to produce any change of colour, promise to give additional value to this process by a thermometer. The knife edges attached to the pendulum described by Capt. Kater,* were forged by Mr Stodart, from a piece of fine wootz. They were carefully hardened, and tempered in the bath at 430° ; on trial they were found too soft. They were a second time hardened, and then heated to 212° . The intention was to increase the heat from that point, trying the temper at the advance of about every ten degrees. In the present instance this was not necessary, the heat of boiling water proving to be the exact point, at which the knife edges were admirably tempered.

It is highly probable that steel, for many uses, may be sufficiently tempered in a range so extensive as from 212° to 430° , and by the thermometer, all the intervening degrees may certainly be ascertained.

That the colour produced on the surface of heated steel is the effect of oxidation, is proved from the circumstance that when steel is heated and suffered to cool under mercury or oil, none of the colours appear: nor do they when it is heated in hydrogen or nitrogen.

Steel admits of being alloyed with several other metals, and the alloys, as appears from a recent investigation of Messrs. Stodart and Faraday† are applicable to various uses.

SECTION XII. Zinc.

1281. Zinc is found in the state of oxide and of sulphuret. It may be obtained pure by dissolving the zinc of commerce in dilute sulphuric acid, and immersing a plate of zinc for some hours in the solution, which is then filtered, decomposed by sub-carbonate of potassa, and the precipitate ignited with charcoal in an iron or earthen retort.

* *Phil. Trans.* 1818, p. 38.

† *Phil. Trans.* 1822, and *Boston Jour. Philos.* i. 130.

Alloys.

Method of
obtaining
pure zinc.

Common zinc, known in commerce by the name of *spelter*, generally contains a portion of lead, copper, iron, traces of arsenic and manganese, and a little plumbago: these impurities remain in the form of a black powder when it is dissolved in dilute sulphuric acid.

Zinc is a bluish white metal, its specific gravity varies from 6,8 to 7,1, it is malleable at 300°, but very brittle when its temperature approaches that of fusion, which is about 680°. It is somewhat ductile, but its wire possesses little tenacity.

1282. *Oxide of Zinc* is obtained by heating the metal exposed to air.* At a red heat it takes fire, burns with a bright flame, and is converted into a white flocculent substance, formerly called *pompholix*, *nihil album*, *philosopher's wool*, and *flowers of zinc*. This oxide, however, when once deposited, is no longer volatile; but if exposed to a violent heat, runs into glass. It has been examined with much attention by Proust, who found it to consist of 80 parts of zinc and 20 oxygen. Gay-Lussac† and Berzelius‡ have since investigated it, and agree in considering it as composed of

| | | |
|----------------|-------|--------|
| Zinc | 80,39 | 100 |
| Oxygen | 19,61 | 24,4 |
| | <hr/> | <hr/> |
| | 100, | 124,4. |

Composition.

The equivalent number deducible for zinc from the composition of the oxide, is 33, but Dr Thomson has been led to conclude that 42 represents its atomic weight, and $42 - 8 = 34$ that of the metal. This number is a mean between the numbers deducible from the experiments of Berzelius and Brande. We may consider oxide of zinc as composed of 1 atom zinc = 34 + 1 oxygen 8. H. 2. 15.

Equivalent number.

This oxide is white, tasteless, and soluble in the alkalis. As prepared by combustion it contains small particles of the metal, which always render it gritty; hence, for pharmaceutical use, it is best prepared by precipitating solution of sulphate of zinc by ammonia, and washing and drying the precipitate. It is sometimes used as a pigment, both with oil and water; and is employed in medicine as a tonic, and as an external application.

1283. Zinc decomposes water very slowly at common temperatures, requiring, probably, the access of air; but acts with

Decomposes water.

* It is by no means easy to obtain pure oxide of zinc. M. Hermann has proposed the following process: Dissolve oxide of zinc or metallic zinc in excess of sulphuric acid, filter the solution, and pass through it sulphuretted hydrogen so long as a brown or yellow precipitate is formed, cadmium, lead, or copper, being thus separated, and the solution filtered, it is to be treated with solution of the chloride of calcium, by which any iron or manganese will be separated. The solution again filtered, is to be crystallized in porcelain vessels, by which sulphate of lime is rejected, and a mother liquor separated which usually contains cobalt and nickel. The crystals of sulphate of zinc are to be dissolved in as small a quantity of cold water as possible, and the sulphate of lime filtered out; then, the solution being rendered more dilute, is to be decomposed by carbonate of soda in slight excess, and the precipitate well washed, dried, and heated to redness is a pure white oxide.—*Bull Unv. A. viii. 263.*

† *Ann. de Chim.* 80, 170.

‡ 81 *Ditto*.

great rapidity, if the vapour of water be brought into contact with it when ignited. In whatever way it is oxidized, we obtain the compound already described, which is the only known oxide of zinc. H.*

Chloride.

1284. *Chloride of Zinc* is formed by heating leaf zinc in chlorine, or by evaporating muriate of zinc to dryness and heating the residue red-hot in a glass tube. The compound is fusible under a dull red heat, and, on cooling, goes through several degrees of consistency, being viscid before it becomes solid. It is very deliquescent, and produces a *muriate of zinc* by the action of water. It appears from the analysis of Dr Davy to consist of equal weights of chlorine and zinc. It was formerly called *butter of zinc*.

If the application of heat be stopped at the right point, Dr Thomson finds that a muriate of zinc may be obtained perfectly free from water, of which this compound and muriate of ammonia are the only examples. It consists of 1 atom oxide of zinc 42, and 1 atom of muriatic acid 37, and its atomic weight is 79.†

The attraction of zinc for chlorine is very great, and this metal may therefore often be employed for separating chlorine from other combinations.

Muriate.

1285. *Muriate of Zinc*.—Muriatic acid, a little diluted, acts on zinc, and evolves hydrogen gas of great purity. The solution is clear, but cannot be brought to crystallize by evaporation. When rapidly evaporated, the muriatic solution yields a thick extract, which has somewhat of the viscosity of bird-lime. This, if still more heated, becomes chloride of zinc.

Action of
water,

1286. Muriate of zinc in strong solution, deposits oxide on adding water, and on being filtered and further diluted, more oxide separates. Weak solutions, when concentrated by evaporation, dissolve the oxide, which will precipitate again, on dilution. The solution is always slightly acid, and ammonia, when added, does not render it neutral, until all the oxide of zinc is precipitated.‡ § H. 2. 18.

Of ammonia.

1287. Liquid ammonia readily dissolves oxide of zinc, and even acts upon the metal. The concentrated solution of the oxide furnishes feathery crystals; it is decomposed by the acids, and the immersion of a plate of copper causes a precipitation

* When Pulverized Zinc is added to fused nitre, or projected with that salt into a red-hot crucible, a very violent detonation takes place; the Zinc is oxidized and part of the oxide combines with the alkali forming a soluble compound. U.

† *First Prin.* ii. 224.

‡ *Quart. Jour.* vi. 159.

§ *Iodide and Zinc* readily combine, and produce a fusible and volatile compound, which, when exposed to air, deliquesces into *hydriodate of zinc*.

When this salt is mingled with perchloride of mercury, a precipitate is obtained of a beautiful bright red colour. When iodate of potassa is added to solution of sulphate of zinc, it forms an insoluble iodate of zinc.

Nitrate.

Nitrate of Zinc.—Nitric acid, moderately strong, acts on zinc with great violence. The solution, by evaporation, crystallizes in four-sided prisms, and affords a deliquescent salt, copiously soluble in water and alcohol, and consisting of 1 atom acid, 1 base and 6 water.

of a part of the zinc, the ammonia acquiring at the same time a blue colour.*

1288. *Sulphuret of Zinc* exists native under the name of *Sulphuret Blende*. It may be formed artificially by heating oxide of zinc with sulphur, and is then of a yellow brown colour.†

Blende is a brittle soft mineral, of different shades of brown and black. Its primitive form is the rhombic dodecaëdron. It usually contains traces of iron and lead. It is an abundant mineral, and important as a source of the pure metal, which is obtained by roasting the ore, and afterwards exposing it to heat in proper distillatory vessels, mixed with charcoal. The English miners call it *black jack*. It has been analyzed by Dr Thomson and found to consist of zinc 67,19 + sulphur 32,81 = 100.‡

1289. *Sulphate of Zinc*.—Zinc readily dissolves in diluted sulphuric acid, with the exception of a small quantity of black powder, which Vogel found to be composed of charcoal, iron, and sulphate of lead. The acid during its action on this metal evolves hydrogen gas; (371) and the gas, when obtained, besides other impurities, holds in combination a portion of the metal.§

1290. When the solution of zinc in sulphuric acid is evaporated, it shoots into crystals which are right rhombic prisms.|| This salt is soluble in 2,5 parts of water at 60, and its solution is not precipitated by any other metal.

If the solution be too much concentrated by evaporation, it deposits, while still hot, an opaque crust on the bottom of the vessel, which is less soluble than the crystals, and is in fact the same as the *white vitriol* of the Germans.¶ Both salts agree in taste, and redden vegetable blues. The crystals formed from a cold solution consist of

| | | | | | | | |
|----------------|-------|----|---|-------|---|-----|------------------------|
| Sulphuric acid | 27,58 | or | 1 | atom | = | 40 | Composition. |
| Oxide of Zinc | 28,96 | " | 1 | " | = | 42 | |
| Water . . . | 43,46 | " | 7 | atoms | = | 63 | |
| <hr/> | | | | | | 100 | Weight of its atom 145 |

* De Lassone, *Ann. de Chim.* xxxv. 53.
† Mr E. Davy, by passing the vapour of sulphur over melted zinc, obtained a white crystalline substance, resembling the natural compound of zinc and sulphur, which is called *phosphorescent blende*.

‡ *Hyposulphite of Zinc* is formed by digesting metallic zinc in sulphurous acid, sulphuretted hydrogen is disengaged, and by gentle evaporation crystals are obtained, which are to be digested in alcohol; this liquid dissolves the hyposulphite, and affords it in prismatic crystals. A mixture of oxide of zinc and sulphur treated by sulphurous acid affords the same salt; it is efflorescent, and easily decomposed by heat.—Fourcroy, *Système des connaissances Chymiques*, v. 380.

Sulphite of Zinc is easily formed by dissolving the oxide in sulphurous acid; it is more easily crystallizable than the hyposulphite and is insoluble in alcohol.

§ Hydrogen gas, holding zinc in solution, may be obtained by a process of Vauquelin. A mixture of the ore of zinc, (blende, or calamine) with charcoal, is to be put into a porcelain tube, which is to be placed horizontally in a furnace, and, when red-hot, the vapour of water is to be driven over it. The gas produced is a mixture of carbonic acid, carburetted hydrogen, and a solution of zinc in hydrogen gas, which has been called *hydrozincic gas*. The zinc is deposited on the surface of the water, over which this gas is kept; but if burned when recently prepared, the gas exhibits, in consequence of this impregnation, a distinctly blue flame.

|| Brooke, in *Ann. Philos.* ¶ Thomson, i. 59, and ii. 353.

The deposit from a hot solution (white vitriol) consists of

Composition.

| | | | | | | |
|----------------|-------|----|---|-------|---|----|
| Sulphuric acid | 36.7 | or | 1 | atom | = | 40 |
| Oxide of Zinc | 38.54 | " | 1 | " | = | 42 |
| Water . . . | 24.76 | " | 3 | atoms | = | 27 |

100 Weight of its atom 109 H. 2. 17.

Sulphate of zinc is prepared for the purposes of the arts from the native sulphuret, and is usually in the form of a white amorphous mass, called *white vitriol*.

Native Sulphate of Zinc is found in places where the sulphuret of zinc occurs; it is probably the result of the decomposition of that ore.*

Carbonate.

1291. *Carbonate of Zinc* occurs native, forming one of the varieties of the mineral called *calamine*. It may be formed by adding carbonate of potassa to sulphate of zinc. It is white and tasteless. It is often found investing carbonate of lime, which has sometimes been decomposed, and the calamine remains in pseudo-crystals.

Process for obtaining zinc from its ores.

1292. The zinc of commerce is procured from the native sulphuret and from calamine by the following process.

The ore is first picked and broken into small pieces, and then submitted to a dull red heat in a reverberatory furnace, by which carbonic acid is driven off from the calamine, and sulphur from the blende. It is then washed, ground, and thoroughly mixed with about one eighth its weight of powdered charcoal. This mixture is put into large earthen pots, not unlike oil jars, six of which are usually placed in a circular furnace; each pot has an iron tube passing from its lower part, through the floor of the furnace, and dipping into water, they are every where else firmly luted: upon the application of a red heat, the metal distills through the tube into the water beneath, whence it is collected, melted, and cast into cakes.

General properties of salts of zinc.

1293. Ferrocyanate of potassa produces a yellowish white precipitate in solutions of zinc. The salts of zinc are mostly soluble in water, and the solutions are colourless and transparent: they are not precipitated by hydriodic acid. Potassa, soda, and ammonia, form white precipitates, soluble in excess of the alkali, and sulphuric acid. Hydrosulphuret of ammonia, produces a yellowish white precipitate. The soluble phosphates, carbonates, and borates, produce white precipitates.

Alloys.

1294. *Alloys of Zinc*.—With potassium and sodium zinc forms brittle alloys, decomposable by exposure to air and water. With iron it forms a white, and somewhat malleable alloy, which is difficult to form; but if plates of hot iron be dipped into melted zinc, they acquire the appearance of tin-plate.

Phosphuret.

* *Phosphuret of Zinc* is of a whitish colour, and a metallic lustre not unlike lead. It has some malleability, exhales a phosphoric smell, and at a high temperature, burns like common zinc. H.

Phosphate.

Phosphate of Zinc is not crystallizable. It may be obtained by dissolving zinc in phosphoric acid, and evaporation to dryness. A phosphate of zinc is also precipitated upon the addition of phosphate of soda to sulphate of zinc. These salts have not been precisely examined, but it is probable there is a phosphate and a bi-phosphate of zinc.

It has been proposed to apply zinc to the purpose of culinary vessels, pipes for conveying water, sheathing for ships, &c.; but it is rendered unfit for the first object, by the facility with which the weakest acids act upon it, and for the remaining ones, by its considerable though slow oxidation, when exposed to the operation of air and moisture. H. 2. 21.

SECTION XIII. Tin.

1295. The properties of tin must be examined in the state of grain-tin or block tin; what is commonly known by the name of tin, being nothing more than iron plates with a thin covering of this metal. Several varieties of tin are met with in commerce, for the discrimination of which, and the means of judging of their purity, Vauquelin has given useful instructions in the 77th volume of the *Annales de Chimie*, and an interesting account of the ores of tin, and of the processes for extracting the metal in Cornwall, has been given by Mr Taylor in the 5th volume of the *Transactions of the Geological Society of London*. H. 2. 39.

1296. This metal has been known from the remotest ages. It was in common use in the time of Moses, and was obtained at a very early period from Spain and Britain by the Phœnicians.*

The native oxide, found in Cornwall and some other counties, is the principal ore of tin;† the metal is obtained by heating it to redness with charcoal. To obtain pure tin the metal should be boiled in nitric acid, and the oxide which falls down reduced by heat in contact with charcoal in a covered crucible. U. The process is described at length in *AIKIN'S Dictionary*, (*Art. TIN.*) To obtain pure tin.

Tin has a silvery white colour, is considerably harder than lead, scarcely at all sonorous, very malleable, though not very tenacious. Under the hammer it is extended into leaves, called *tin-foil*, which are about $\frac{1}{1000}$ th of an inch thick.‡ Its specific gravity is 7,30. It melts at 442° , and by exposure to heat and air is gradually converted into a grey peroxide. Placed upon ignited charcoal under a current of oxygen gas, it burns very brilliantly. Properties:

1297. A preparation under the name of *powdered tin* is sometimes directed to be prepared for pharmaceutical use, by Powdered tin.

* Pliny, lib. iv. cap. 34, and xxxiv. cap. 47.

† In some of the valleys of Cornwall, tin is found in rounded nodules, of various sizes, mixed with pebbles and rounded fragments of rocks. To separate the tin from the alluvial matter, currents of water are passed over it, and hence these deposits have been called *stream works*, and the tin ore, *stream tin*. A modification of stream tin is called *wood tin*. It usually appears in small banded fragments of globular masses.

‡ The process of making tin-foil consists simply in hammering out a number of plates of the metal, laid together upon a smooth block or plate of iron. The smallest sheets are the thinnest. U.

shaking the melted metal in a wooden box rubbed with chalk on the inside : *tin filings* have also a place in some *Pharmacopœiæ*, and have been used as a vermifuge. These preparations are, however, both dangerous, the metal being rendered poisonous in the former case by slight oxidation,* and often creating very dangerous irritation when given in filings.

Protoxide.

1298. *Protoxide of Tin* is obtained by precipitating proto-muriate of tin by ammonia; it falls in the state of hydrate; when dried, it is of a grey colour, and undecomposable by heat. It dissolves in the alkalies; exposed to heat and air it passes into the state of peroxide, undergoing a faint combustion. Its ammoniacal solution, when long kept, deposits metallic tin in arborescent crystals, and becomes a solution of the peroxide.

Peroxide.

1299. *Peroxide of Tin* is formed by treating the metal with nitric acid : there is a violent action attended by the formation of nitrate of ammonia. (533). Scarcely any of the metal is dissolved, but remains as a yellowish powder, which may be purified by washing. It is also formed by heating tin filings with red oxide of mercury; and by projecting a sufficient quantity of nitre upon red-hot tin. This oxide dissolves in the alkalies. Fused with glass it forms *White Enamel*. Heated intensely, it becomes insoluble in acids, and undergoes fusion.

Composition.

1300. From data furnished by the experiments of Berzelius, Gay-Lussac and Thenard, these oxides are inferred to be thus constituted :—

| | Tin. | | | | | Oxygen. | | | |
|---------------|------|----|---|------|-----|---------|----|---|--------|
| Protoxide . . | 58 | or | 1 | atom | . . | 8 | or | 1 | atom |
| Peroxide . . | 58 | " | 1 | " | . . | 16 | " | 2 | atoms. |

Tin putty.

The substance called *Tin Putty*, is an oxide of tin formed by levigating the crusts of oxide that form upon the metal when kept for some time in fusion.

Proto-chloride.

1301. Tin unites in two proportions with chlorine. The *Proto-chloride*, consisting of 1 atom of tin and 1 atom of chlorine, may be made either by evaporating the muriate of the protoxide to dryness and fusing the residue in a close vessel, or by heating an amalgam of tin with calomel.† It is a grey solid substance, of a resinous lustre, which fuses at a heat below redness, and when heated in chlorine gas is converted into the bichloride.

Bichloride.

1302. *Bichloride of Tin*, composed of 1 atom tin and 2 atoms of chlorine, may be prepared either by heating metallic tin or the proto-chloride in an atmosphere of chlorine, or by distilling a mixture of 8 parts of tin in powder with 24 of corrosive sublimate. It is a colourless, volatile liquid, which emits copious white fumes when exposed to the atmosphere. It has a very strong attraction for water, and is converted by that

* Orfila, *Traité des Poisons*, T. i. 2me partie, p. 18.

† Dr Davy.

fluid into the permuriate. It was formerly called the *fuming liquor of Libavius*.

1303. The *Proto-muriate of Tin*, may be obtained by boiling one part of tin with two of muriatic acid, in a tubulated retort. The solution has always an excess of acid, is perfectly limpid and colourless; and contains the metal at the minimum of oxidation. It has a tendency, however, to acquire a farther proportion of oxygen, and should, therefore, be carefully preserved from contact with the air. This property of absorbing oxygen is so remarkable, that it may even be applied to eudiometrical purposes. Proto-muriate of tin has, also, the property of reducing to a minimum of oxidation, those compounds of iron, in which the metal is fully oxidized, for example, it reduces the red sulphate to the green. It is a test also of gold and platinum, and blackens the solution of corrosive sublimate. With hydro-sulphurets it gives a black precipitate. H.

Proto-muriate.

With solution of gold it produces a purple precipitate used in painting porcelain, and known under the name of *Purple of Cassius*. It crystallizes from its concentrated solution in small deliquescent needles. With infusion of cochineal it produces a purple precipitate. This muriate of tin is the *Sal Jovis* of old writers, Jupiter being the name by which the alchemists distinguished this metal.

Purple of Cassius.

1304. Recent muriate of tin is a very delicate test of mercury. M. Chenevix says, if a single drop of a saturated solution of neutralized nitrate, or muriate of mercury, be put into 500 grs. of water, a few drops of solution of muriate of tin will render it a little turbid, and of a smoke-grey; and the effect is perceptible with ten times as much water. U. 749.

A test of mercury.

1305. The proto-muriate of tin appears to be composed of 1 atom protoxide + 1 atom muriatic acid. H. 2. 44.*

Composition.

1306. When potassa is added to muriate of tin, a *submuriate* of the protoxide is thrown down, consisting, according to Dr Davy of 134 protoxide + 37 acid, or of 1 atom muriatic acid, 2 atoms protoxide and 2 atoms water.

1307. The *Permuriate* of tin forms acicular crystals in the upper parts of the phials containing the bi-chloride imperfectly secured from air. The addition of the pure alkalies to this salt of tin, occasions a precipitate which has not been accurately examined, but is said to be a *subpermuriate*. The peroxide of tin is more readily soluble in alkalies than the protoxide; it has been hence termed *Stannic acid*.†

1308. *Nitro-muriate of Tin*.—The nitro-muriatic acid (formed by mixing two or three parts of muriatic acid and one of nitric,) dissolves tin abundantly, with violent effervescence,

Nitro-muriate.

* On the preparation of muriate of tin, see Berard, *Ann. de Chim.* lxxviii. 78; or Nicholson's *Jour.* xxvi, and Chaudet, *Ann. de Chim. et Phys.* iii. 376.

† *Iodide of Tin* may be formed directly by heating the metal with iodine; or indirectly by adding hydriodic acid to a solution of muriate of tin. It is an orange-coloured compound, and has not been analyzed.

and with so much heat, that it is necessary to add the metal slowly by successive portions. The solution is apt to congeal into a tremulous gelatinous mass; and if water be added, it is partly decomposed, and some oxide separated. The solution, used by the dyers, is prepared with that dilute nitric acid called single aqua-fortis, to each pound of which are added from one to two ounces of the muriate of soda or ammonia. This compound acid is capable of taking up about an eighth its weight of tin. H. 2. 44.

Uses. The solution is employed to heighten the colours of cochineal, gum-lac and some other red tinctures, from crimson to a bright scarlet in the dyeing of woollens.

Nitrate. 1309. *Nitrate of Tin*—When nitric acid, highly concentrated, is poured upon tin filings, very little effect is produced; but when a small quantity of water is added, a violent effervescence follows; and the metal is reduced to a bulky powder, which is the white oxide retaining a little acid. If more water be added, an acid liquor is obtained, holding very little tin in solution, and containing nitrate of ammonia, the alkaline base of which is formed by the simultaneous decomposition of the water and nitric acid, and the union of the hydrogen of the former with the nitrogen of the latter. (533) H. Tin, however, is slowly dissolved, without effervescence, in nitric acid greatly diluted; the solution is yellow and will not crystallize; exposed to air it absorbs oxygen and peroxide of tin precipitates.

Sulphuret. 1310. *Tin and Sulphur*.—Tin unites with sulphur, but requires, for its combination, so high a temperature, that at the moment of union there is too small a quantity of sulphur present, to saturate the tin, and a mechanical mixture results, of tin and sulphuret of tin. The only method of obtaining the saturated sulphuret is to melt the *aurum musivum*, which will presently be described, in close vessels. The *protosulphuret* is of a bluish colour and lamellated structure.

Composition. It is composed, according to Dr John Davy and Berzelius, of 1 proportional metal + 1 sulphur.

Aurum musivum. 1311. The second sulphuret, or *bisulphuret* of tin (*aurum musivum*), is formed by heating sulphur with peroxide of tin, or, by heating in a matrass a powdered amalgam of 12 parts of tin and 6 of mercury, mixed with 7 parts of flowers of sulphur and 6 of muriate of ammonia. A gentle heat is to be applied till the white fumes cease to appear, when the heat is to be raised to redness, and kept so for some time. On cooling, the *aurum musivum* (or *Mosaic Gold*) may be obtained by breaking the matrass. It is of a beautiful gold colour, and flaky in its structure. Proust was of opinion that it is a sulphuretted oxide; but Dr Davy and Berzelius have shown that the tin is in a metallic state. It consists of 1 atom tin + 2 atoms of sulphur. H. 2. 45.

1312. *Aurum musivum* has no taste, is not soluble in water, acids or alkaline solutions. But in the dry way it forms a yel-

low sulphuret, soluble in water. It is used as a pigment for giving a golden colour to small statue or plaster figures. It is likewise said to be mixed with melted glass to imitate lapis lazuli. U. 208. Properties.

1313. *Sulphate of Tin*.—When tin is boiled in sulphuric acid, a solution is obtained which deposits white acicular crystals. A protosulphate of tin is also precipitated by pouring sulphuric acid into protomuriate of tin. If the sulphate be long boiled, a copious white precipitate subsides, which will not again dissolve. It is composed of the white oxide retaining only a small portion of acid, and constituting in fact a sub-sulphate. H.* Sulphate.

1314. The salts of tin are mostly soluble in water. They are precipitated of an orange colour by hydriodic acid, and by hydrosulphuret of ammonia, provided no excess of acid be present. Solution of muriate of gold, and of corrosive sublimate produce purple and black precipitates in the salts of tin containing the protoxide, but none in those containing the peroxide. Ferrocyanate of potassa produces a white precipitate in solution of muriate of tin. A plate of lead frequently throws down metallic tin, or its oxide, from the saline solutions. Characteristics of the salts of tin.

1315. Tin forms useful alloys with many of the metals. *Pewter* is one of these; and the best kind of it is entirely free from lead, being composed chiefly of tin with small proportions of antimony, copper and bismuth.† An amalgam formed by gradually adding three parts of mercury to twelve of tin melted in an iron ladle, and stirring the mixture, is much used in silvering looking glasses. H. With potassium and sodium, tin forms brittle white alloys. Its alloy with manganese is not known. It does not readily combine with iron, but tin-plate may be considered as an imperfect alloy of those metals. With zinc it forms a hard brittle alloy.‡ Alloys.

SECTION XIV. Cadmium.

1316. Cadmium was discovered in the autumn of 1817, by Stromeyer, in an oxide of zinc, which had been prepared for Discovery.

* *Hydrosulphuretted Oxide of Tin* is yellow brown, and formed by pouring solution of sulphuretted hydrogen into dilute muriate of tin. *Phosphuret of Tin* may be formed by dropping phosphorus into melted tin. It is of a silvery colour, sectile, and somewhat ductile. When its filings are sprinkled upon hot coals the phosphorus burns. *Phosphite of Tin* has not been examined. *Phosphate of Tin* is formed by adding phosphate of soda to the solutions of tin. It is a white powder, not soluble in water, and fuses at a red heat into an opaque white enamel. *Carbonate of Tin*—When carbonate of potassa is added to protomuriate of tin, a white precipitate ensues, which, when washed and dried effervesces copiously with the acids. *Borate of Tin* is an insoluble white powder.

† On the alloys of tin, a memoir of M. Dussausoy may be consulted in the 5th vol. of *Ann. de Chim. et Phys.*; and Mr Chaudet's paper in the same, and in the 7th volume.

‡ For a method of bronzing tin see *Quart. Jour.* N. S. 2. 483.

medicinal use from an ore of zinc brought from Silesia.* He ascertained its principal properties and combinations; and has since extracted it from various other ores of zinc.† Dr Clarke has shown that it exists in the ores of zinc from Derbyshire and Mendip, and in the zinc of commerce;‡ and Mr Herapath, of Bristol, has pointed out an abundant source of it in the sublimate, which, in the process for obtaining zinc by distillation, rises before the zinc, in what the workmen call the *brown blaze*. Of this sublimate, which is attached to the roof of the vault, it forms from 12 to 20 per cent.§

Method of
detecting
cadmium

1317. The presence of cadmium, in an ore of zinc suspected to contain it, may be discriminated by directing the blue flame of a candle upon a small fragment placed on a slip of platinum foil. If any cadmium be present, its oxide will be reduced, volatilized, and carried along the slip of platinum, coating it with its peculiar reddish-brown oxide. Dr Wollaston, to detect cadmium, dissolves the ore of zinc in muriatic acid, gets rid by heat of the excess of acid, and adds distilled water. All the metals that iron will precipitate he removes by a rod of iron, and filters the liquor into a platinum capsule containing a piece of zinc. The cadmium, if any be present, will coat over the surface of the capsule with a precipitate of a dull leaden hue, and will adhere so firmly that it may be washed, and thus freed from any remaining solution of zinc. Muriatic acid will dissolve the lead-coloured precipitate with effervescence, and either carbonated or caustic potassa will yield a white precipitate; which may be tested before the blow-pipe in the manner already described.

Of separating
from zinc
ores.

1318. To separate cadmium from the ores of zinc, Stromeyer dissolves the ore in sulphuric acid; and through the solution, which ought to contain an excess of acids, sends a current of sulphuretted hydrogen gas. The precipitate is well washed, dissolved in concentrated muriatic acid, and the excess of acid expelled by evaporation. The residue is dissolved in water, and precipitated by carbonate of ammonia, an excess of which must be added to re-dissolve any zinc or copper that may have been thrown down by the sulphuretted hydrogen gas. Carbonate of cadmium alone remains, which, after being heated to drive off the carbonic acid, is reduced by mixing it with lamp-black, and exposing it to a moderate red heat in a glass or earthen retort.

Properties.

1319. Cadmium resembles tin very nearly in colour, lustre, and in the sound it emits when bent. It is somewhat harder than tin, and surpasses it in tenacity. It is very ductile, and may be reduced to fine wire, or thin plate; yet when long beaten, it scales off in different places. Its specific gravity is 8,604 before hammering, and 8,694 afterwards; or, according

* Iodine has lately been found in this ore.—*Edin. Jour.* Jan. 1828.

† *Ann. Philos.* xiv. 269.

‡ *Ann. Philos.* xv. 272, and N. S. iii. 123.

§ *Ibid.* 435.

to Mr Children,* 8,67 before, and 9,05 after being hammered. It melts at a heat below redness, and is volatilized by a heat not much greater than that required to vaporise mercury. Its vapour has no odour. It condenses in drops as readily as mercury, and these, on congealing, present distinct traces of crystallization.

1320. Cadmium is as little altered by exposure to the air as tin. When heated in the open air, it burns as readily as the latter metal, and is converted into a brownish-yellow oxide. This oxide, which is its only one, consists of 100 metal + 14,352 oxygen;† which gives 56 for the equivalent number of the metal, and 64 for that of the oxide. This oxide is soluble in ammonia, but not in carbonate of ammonia, or in potassa, or its carbonate, which even precipitate it from its solution in ammonia. By availing himself of this property, Mr Children separated it from oxide of zinc, which is not thrown down by the fixed alkali, and thus verified its presence in compounds containing much zinc and little cadmium.

1321. With the acids, oxide of cadmium unites and forms salts, which agree in the following characters. Fixed alkalies throw down a white hydrated oxide, as does ammonia, with this difference, that the latter, added in excess, re-dissolves the precipitate. Prussiate of potassa causes a white sediment, as does oxalate of ammonia. Sulphuretted hydrogen, and the hydro-sulphurets, throw down cadmium of a yellow or orange colour, like orpiment. No change is produced by chromate of potassa, succinate or benzoate of ammonia, infusion of galls, or sulphate of soda.

1322. *Chloride of Cadmium* crystallizes in small rectangular prisms, perfectly transparent, which effloresce when heated, and are very soluble. At a high temperature, it sublimes in small micaceous plates: 100 parts of the fused chloride consists of 38,61 chlorine + 61,39 metal. This gives 57 for the equivalent of cadmium, differing very little from the number deduced from the oxide.‡

1323. Cadmium unites with sulphur, as with oxygen, in only one proportion, which is that of 100 metal to 28,172 sulphur. The *sulphuret* has a yellow colour with a shade of orange. Concentrated muriatic acid acts readily upon it, and evolves sulphuretted hydrogen gas. The sulphuret may be formed by

* *Quart. Jour.* vi. 226.

† Stromeyer.

‡ *Iodide of Cadmium* forms large and beautiful hexaëdral tables, of a metallic or pearly lustre. At high temperatures, the iodine escapes. It consists of 100 metal + 227,43 iodine.

Nitrate of Cadmium crystallizes in prisms or needles, which are deliquescent. Its constituents are 100 acid + 117,58 oxide. The *sulphate* crystallizes in large rectangular prisms resembling sulphate of zinc, which are very soluble in water. They effloresce in the air, and at a gentle heat lose their water of crystallization, amounting to 34,26 on 100 of the dry salt. The neutral sulphate consists of 100 acid + 161,12 oxide.

The *Carbonate* is pulverulent and insoluble in water, and readily decomposable by heat. It consists of 100 acid + 292,88 oxide. *Phosphuret* of cadmium has a grey colour and a feeble metallic lustre.

The *phosphate* is pulverulent and insoluble. It is constituted of 100 acid + 225,49 oxide.

heating sulphur either with the metal or the oxide, or by precipitating a solution of cadmium by sulphuretted hydrogen.

Alloys.

1324. Cadmium unites with other metals. Its alloy with copper is white, with a slight tinge of yellow. It unites also with cobalt, platinum, and mercury, and probably with other metals.

Equivalent number.

From a survey of its salts, it appears that their analysis does not lead to a perfect agreement as to the equivalent of its oxide, and consequently of that of the metal. None of the results, however, are very remote from affording 64 for the number representing the oxide, from which deducting 8, we obtain 56 for the equivalent of cadmium. H. 2. 49.

SECTION XV. *Copper.*

Pure copper, how obtained.

1325. This metal is found native, and in various states of combination. Of its ores, the oxide, chloride, sulphuret, sulphate, phosphate, carbonate, and arseniate, are the most remarkable. The metal may be obtained perfectly pure by dissolving the copper of commerce in muriatic acid; the solution is diluted and a plate of iron immersed, upon which the copper is precipitated. It may be fused into a button, after having been previously washed in dilute sulphuric acid to separate a little iron that adheres to it.

It was known in the early ages of the world, and was the principal ingredient in domestic utensils, and in the instruments of war, previous to the discovery of malleable iron.*

Properties.

1326. Copper has a fine red colour, and much brilliancy; it is very malleable and ductile, and has a peculiar smell when warmed or rubbed. It melts at a cherry red or dull white heat. Its specific gravity is 8,90. Under a flame urged by oxygen gas, it takes fire, and burns with a beautiful green light.

Action of air

1327. Copper is oxidized by air. This may be shown by heating one end of a polished bar of copper, which will exhibit various shades of colour, according to the intensity of the heat.

A plate of copper, exposed for some time to heat, becomes covered with an oxide, which breaks off in scales when the copper is hammered. It is composed of 62 of the black oxide and 38 copper. This oxide, when exposed on a muffle, is farther oxidized, and assumes a deep red hue. Copper is also oxidized by long exposure to a humid atmosphere, and assumes a green colour; but the green compound holds carbonic acid in combination. The oxides of copper do not return to a metallic state by the mere application of heat; but require, for their reduction the admixture of inflammable matter.

* The word *copper* is derived from the island of Cyprus, where it was first wrought by the Greeks.

1328. *Native Copper* occurs in a variety of forms; massive, dendritic, granular, and crystallized in cubes, octoëdra, &c. It is found in Cornwall, Siberia, and other parts of Europe. Large masses have been found in various parts of America; one of which, about 30 miles from Lake Superior, described by Mr Schoolcraft, weighs by estimation 2,000 lbs.*

1329. *Copper and Oxygen*.—Copper is susceptible of only two degrees of oxidizement; in its lower stage the compound is red; when oxidated to the maximum, it is black. The red or *Protoxide* occurs native. It may be formed artificially, by the following process. Mix together $57\frac{1}{2}$ parts of black oxide of copper, precipitated from the sulphate on an iron plate. Triturate it in a mortar, and put the mixture with 400 parts of muriatic acid, into a phial, which is to be well stopped. The copper and its oxide will be dissolved with heat. When potassa is poured into this solution, the oxide (or rather hydrated protoxide) of copper is precipitated of an orange colour.† This oxide, when deprived of water, becomes red; but it attracts oxygen so strongly that it can scarcely be dried without absorbing more. It is composed of

| | | | | | | | | | | |
|--------|---|---|---|---|-------|---|---|---|---|------|
| Copper | : | : | : | : | 88,89 | : | : | : | : | 100. |
| Oxygen | : | : | : | : | 11,11 | : | : | : | : | 12,5 |

Composition.

100.

1330. The equivalent number of copper, deducible from the composition of the protoxide, is therefore 64, for $12,5 : 100 :: 8 : 64$, and the protoxide will consist of 1 atom copper = 64 + 1 atom of oxygen 8 = 72, and the peroxide of 1 copper + 2 oxygen = 80.

The *Ruby Copper* of mineralogists is a native Protoxide.

1331. *Peroxide* of Copper may be obtained, either by calcining the scales of copper, which have already been alluded to, under a muffle; or by decomposing nitrate of copper by carbonate of potassa, and igniting the precipitate; or by the simple ignition of the nitrate.

It varies in colour from a dark brown to a bluish black, according to the mode of its formation. It undergoes no change by heat alone, but is readily reduced to the metallic state by heat and combustible matter. It is insoluble in water, combines with nearly all the acids, and most of its salts have a green or blue tint. It is soluble in ammonia, forming with it a deep blue solution, a property by which the peroxide of copper is distinguished from all other substances.

1332. *Copper and Chlorine*. Gaseous chlorine acts upon copper with great energy, and produces two chlorides; the one a fixed fusible substance, which is the protochloride, consisting of 1 proportional of copper = 64 + 1 proportional of chlorine = 36. The other a volatile yellow substance, which is a perchloride, and contains 2 proportionals of chlorine.

* See other localities in Cleaveland's *Minerology*, p. 554.

† Chenevix.

Proto chlor-
ide, how ob-
tained.

1333. The *Protochloride of Copper* was first described by Boyle in 1666, under the name of *Rosin of Copper*. It may be obtained by exposing copper filings to the action of chlorine not in excess; or by evaporating the proto-muriate, and heating the residue in a vessel with a very small orifice; or by heating the perchloride in the same way. It is also the residue of the distillation of a mixture of two parts of corrosive sublimate and one of copper filings. It is insoluble in water, but soluble in muriatic acid, from which potassa throws down a protoxide. When water is added to its muriatic solution it is precipitated unaltered; its colour varies, being generally dark brown; but if fused and slowly cooled, it is yellow, translucent, and chrysalline.

Perchloride.

1334. *Perchloride of Copper* may be formed by dissolving peroxide of copper in muriatic acid, and evaporating to dryness by a heat below 400° . It is soluble in water, producing a permuriate, from which potassa precipitates the peroxide: its colour is yellow, but it becomes white and afterwards green, when exposed to heat and moisture. Exposed to a red heat in a tube with a very small orifice, gaseous chlorine is expelled, and it becomes a protochloride.

Action of mu-
riatic acid.

1335. Muriatic acid acts with difficulty on metallic copper, except it be concentrated and boiling; but it readily dissolves the peroxide, forming a brown or grass-green solution, according to its state of dilution. This is a *permuriate of copper*. If plates of copper be exposed to the joint action of air and the fumes of muriatic acid, they become encrusted with a green powder which is readily soluble in muriatic acid, and which is a true *muriate*, or compound of 1 atom of base + 1 atom of acid.

Protomuri-
ate.

If metallic copper be digested in muriatic acid with the peroxide, an olive-coloured solution of *proto-muriate of copper* is formed, which strongly attracts oxygen, and which, when concentrated, deposits small grey crystals. This salt is decomposed by merely pouring it into water. The addition of potassa occasions a precipitate of the orange or protoxide of copper.

Native sub-
muriate, or
atacamite.

1336. *Native Sub-muriate of Copper* is found in Peru and Chili, sometimes in the form of green sand, and sometimes massive and chrysallized. The green sand was found in the river Lipas, in the desert of Atacama, separating Peru from Chili, hence mineralogists have termed this variety, *Atacamite*.* It is of a deep green colour, and contains, according to Dr Davy's analysis, 73 peroxide of copper + 16,2 muriatic acid + 10,8 water.† It is a submuriate of copper that is formed by the action of sea-water upon copper sheathing. (262.)

* Muriate of copper has also been found upon some of the lavas of Vesuvius.

† *Chlorate of Copper* is a blue-green deliquescent salt, difficultly chrysallizable, formed by dissolving peroxide of copper in chloric acid. A piece of paper dipped into its solution burns with a remarkable green flame.—Vauquelin. An *Iodide of Copper* is precipitated from solutions of the metal by hydriodic acid. It is brown and insoluble. When solution of the alkaline iodates is added to solutions of copper an insoluble *iodate of copper* is thrown down.

1337. *Nitrate of Copper.* Nitric acid, diluted with three parts of water, rapidly peroxidizes copper, evolving nitric oxide, and forming a bright blue solution, which affords deliquescent prismatic crystals on evaporation, of a fine blue colour and very caustic. It consists of 80 peroxide + 108 acid; but the crystals contain a considerable portion of water, which causes them to liquefy at a temperature below 212° . At a higher temperature they lose water and acid, and according to Proust become a *sub-pernitrate*, which is insoluble in water, and entirely decomposed at a red heat. There appears to be no protonitrate of copper, for protoxide of copper, digested in very dilute nitric acid is resolved into peroxide which dissolves, and into metallic copper. Potassa forms, in this solution, a bulky blue precipitate of *hydrated peroxide of copper*, which when boiled in potassa or soda, becomes black from the loss of its combined water.

Nitrate.

Hydrated peroxide.

1338. When crystals of nitrate of copper are coarsely powdered, sprinkled with a little water, and quickly rolled up in a sheet of tin-foil, there is great heat produced, nitrous gas is rapidly evolved, and the metal often takes fire.

Exp.

1339. If ammonia be added to solution of nitrate of copper, it occasions a precipitate of the hydrated peroxide; but if it be added in excess, the precipitate is re-dissolved, and a triple *ammonio-nitrate of copper* is produced.*

Ammonio-nitrate.

1340. If peroxide of copper be digested in ammonia it is dissolved, forming a bright blue solution, which by careful evaporation, affords fine blue crystals. A mixture of lime, sal-ammoniac, and water, placed in a copper vessel, or mixed with oxide of copper, also affords a fine blue liquor, in consequence of the action of the ammonia on the oxide of copper. This solution is the *Aqua Sapphirina* of old pharmacy. The compound has sometimes been called *Ammoniuret of Copper*, or *Cuprate of Ammonia*.

Ammoniuret of copper.

1341. The protoxide of copper also dissolves in ammonia, but the solution is colourless; if it be exposed to air it becomes blue.

This may be well shown by filling a tall glass with liquid ammonia, and adding a few drops of solution of proto-muriate of copper: the liquid presently acquires a blue colour upon the surface, but remains for some time colourless below.

Exp.

Into a half ounce stoppered phial, filled with a solution of ammonia, drop a few pieces of metallic copper; if the bottle be left unstopped, a beautiful blue liquid will be obtained; if the stopper be replaced, this colour in a short time will disappear, and re-appear on again admitting the air. In this manner a blue and colourless liquid can be alternately produced as we withdraw or replace the stopper.

Exp.

In this experiment the peroxide when excluded from the air, is converted into a protoxide by the action of the metallic cop-

* A *sub-nitrate* of copper is also described by Berzelius, (82 *Ann. de Chim.*) it is obtained by adding a small portion of potassa to the solution of the nitrate, or by heating the dry salt gently.

per, which again becomes the peroxide by the action of the atmosphere.

Brunswick
green.

1342. Plates of copper digested in a solution of muriate of ammonia, are soon incrustated with a green powder, which has been used in the arts under the name of *Brunswick green*.*

Sulphurets.

1343. *Copper and Sulphur*. There are two sulphurets of copper, both of which exist native; the one is black and may be formed artificially, by mixing together 8 parts of copper filings, and 2 of sulphur, and exposing the mixture to a gentle heat.† Whenever the sulphur is raised a little above its melting temperature, combustion suddenly pervades the whole mass with explosive violence, exceeding in brightness that produced by the fusion of iron and sulphur. The experiment succeeds equally well *in vacuo* or in azote. U. 370.‡

Exp.

Copper leaf, Berzelius observes,§ burns in gaseous sulphur, as brilliantly as iron wire in oxygen gas. A compound is formed, precisely analogous to the native black sulphuret of copper, or *copper glance*. It is a *proto-sulphuret*, and consists of 1 atom copper + 1 sulphur.

Bi-sulphuret.

1344. Bi-sulphuret of copper forms the principal ingredient of *copper pyrites*, or the yellow sulphuret, which is the most important and generally occurring ore, affording the largest proportion of the copper of commerce. It consists of 1 atom copper + 2 atoms of sulphur.||

Sulphite.

1345. *Sulphite of Copper* may be obtained by passing a current of sulphurous acid gas (which has been first passed through

* According to Dr Mac Culloch a solution of copper in ammonia may be obtained by boiling metallic copper in water of ammonia. The water is decomposed, the metal is oxidated and hydrogen escapes. Advantage may be taken of this in cleaning (or colouring, as it is termed by jewellers) gold trinkets, such as chains, &c. which are often made of a very inferior alloy. Artists make use of weak nitric acid, or of the materials from which the acid is produced, and which often destroys the finer kinds of workmanship by dissolving the copper of the alloy to some depth on the surface; the gold not being acted upon, the trinket appears as if newly gilded. Boiling in ammonia is a safe substitute for this process, and the operation may be performed by any person without the assistance of the artist. Brewster's *Jour.* i. 75. *Bost. Jour.* ii. 206.

† Or by mixing 3 parts of the metal with 1 of sulphur, in a glass tube.

‡ From this experiment, Dr Ure remarks, we are entitled to consider sulphur as a true supporter of combustion, if this name be retained in chemistry,—and sulphur is at once a supporter and a combustible in the fullest sense; a fact fatal to this technical distinction, since one body cannot be possessed of diametrically opposite qualities. U. 370.

§ 79 Ann. de Chim. 250. See also Vauquelin on the artificial Sulphuret of Copper, lxxx. 265. Berzelius states that 100 metal combine with 25.6 sulphur.

The Cornish mines are very productive of this ore, and it is the principal product of the Parys mountain mine in Anglesea.

The following is an outline of the process by which these ores of copper are reduced, as carried on upon a very large scale near Swansea, where the chief part of the Cornish ores are brought to the state of metal. The ore, having been picked and broken, is heated in a reverberatory furnace by which arsenic and sulphur are driven off. It is then transferred to a smaller reverberatory, where it is fused, and the slag which separates, being occasionally removed, is cast into oblong masses used as a substitute for bricks. The impure metal collected at the bottom of the furnace is granulated by letting it run into water; it is afterwards re-melted and granulated two or three times successively, in order further to separate impurities, which are chiefly sulphur, iron, and arsenic, and ultimately cast into oblong pieces called *pigs*, which are broken up, roasted, and lastly melted with a portion of charcoal in the refining furnace. It is now malleable: and is generally rolled into plates, which are annealed, and when hot, quenched in urine, which gives the metal a peculiar red tinge. B.

a small quantity of water, in order to deprive it of sulphuric acid) into a vessel containing water and peroxide of copper. A green liquid is formed, which contains sulphite of copper, with a large excess of acid; and sulphite of copper in very small red crystals, remains at the bottom of the vessel. This salt has been investigated by Chevreul,* and found to consist of protoxide of copper 63,84 sulphurous acid 36,16. H.

1346. *Persulphate of Copper.—Roman Vitriol.—Blue Vitriol.*—This salt is formed by dissolving peroxide of copper in sulphuric acid. It crystallizes in rhomboidal prisms of a fine blue colour, doubly refractive, and soluble in about 4 parts of water at 60°. It may also be formed by boiling copper filings in sulphuric acid; a process which furnishes abundance of sulphurous acid, but which is not generally had recourse to, to produce sulphate of copper. It is made upon a large scale, by exposing roasted sulphuret of copper to air and moisture. When heated it loses water of crystallization, and at a higher temperature sulphuric acid is evolved, unmixed with sulphurous acid, as in the case of the decomposition of proto-sulphate of iron, and peroxide of copper remains. It is the *Vitriol* or *Salt of Venus* of the alchemists. It consists of 80 peroxide + 80 sulphuric acid, when crystallized it contains 10 atoms of water, and consequently its composition will stand thus:—

Persulphate,
or Blue Vitri-
ol.

Composition.

1 atom of peroxide, 2 atoms of sulphuric acid, 10 atoms of water.

Strictly speaking this salt is a bi-sulphate.

There appears to be no *proto-sulphate* of copper, for when protoxide of copper is digested in dilute sulphuric acid, metallic copper is separated, and a solution of the peroxide obtained.

1347. By cautiously adding ammonia to a solution of the foregoing salt, a *subsulphate of copper* is precipitated, consisting of 2 atoms peroxide + 1 acid. The alkalies precipitate hydrated peroxide from the solution of the persulphate, and excess of ammonia forms a *triple sulphate of ammonia and copper*. The same compound is formed by triturating carbonate of ammonia with crystals of sulphate of copper. It is the *cupri ammoniaretum* of the U. S. Pharmacopœia.†

Subsulphate.

1348. Phosphoric acid unites with peroxide of copper in two proportions. If solutions of phosphate of soda and sulphate of copper be mingled together, a bluish green precipitate is formed, consisting of

Phosphate.

1 atom peroxide of copper, 2 atoms phosphoric acid, 1 atom water.

It is therefore a *bi-phosphate*. The *phosphate* has not yet been formed artificially, but has been found native, of an emerald green colour. H.‡

* Ann. de Chim. 88. 181.

† *Sulphate of Copper and Potassa* is a triple salt formed by digesting peroxide of copper in bi-sulphate of potassa. It crystallizes in rhomboids of a pale blue colour. *Phosphorus and Copper* form a grey brittle phosphuret. It is most easily made by dropping pieces of phosphorus on red-hot copper wire. It is more fusible than copper.

‡ See Cleaveland's Mineralogy, 574.

Carbonate.

1349. *Carbonate of Copper*, artificially prepared, by adding carbonate of potassa to sulphate of copper and drying the precipitate, is a green compound, insoluble in water, consisting, according to Mr R. Phillips, of 80 peroxide + 22 carbonic acid + 9 water. Copper, exposed to damp air, becomes incrustated with this compound. Exposed to heat, it loses water and carbonic acid, and leaves the peroxide. In order to heighten the green tint for which this compound is esteemed as a pigment, it should be repeatedly washed with boiling water.

Verditer.

1350. There is a fine blue cupreous preparation, called *Refiner's Verditer*, principally made by silver refiners. It consists, according to Mr R. Phillips, of 3 proportionals of oxide, 4 of carbonic acid, and 2 of water.* There is a very inferior pigment, also called Verditer, which is a mixture of subsulphate of copper and chalk.

According to Pelletier, a good verditer may be obtained as follows: add a sufficient quantity of lime to nitrate of copper to throw down the hydrated oxide; it gives a greenish precipitate that is to be washed and nearly dried upon a strainer; then incorporate it with from 8 to 10 per cent. of fresh lime, which will give it a blue colour, and dry it carefully.

Native.

1351. *Native Carbonate of Copper* is found of a green and blue colour. The former, or *Malachite*, is found in various forms, but never regularly crystallized. It is of various shades of green, and often cut into small slabs, or used as beads and brooch stones. The pulverulent variety has been termed *crysocolla* and *mountain green*.†

Alloys.

1352. Many of the *alloys* of copper are important. With gold it forms a fine yellow ductile compound, used for coin and ornamental work. British sterling or standard gold consists of 11 gold + 1 copper. The specific gravity of this alloy is, 17,157. With silver it forms a white compound, used for plate and coin. [See *Gold* and *Silver*.] Lead and copper require a high red heat for union; the alloy is grey and brittle.

Of the alloys of copper with the metals already described the most important are brass and bell-metal. It forms white compounds with potassium and sodium; a reddish alloy with manganese; and a grey one with iron.

1353. *Brass* is an alloy of copper and zinc. The metals are usually united by mixing granulated copper with calamine (1291) and charcoal: the mixture is exposed to heat sufficient to reduce the calamine and melt the alloy, which is then cast into plates. The relative proportions of the two metals vary in the different kinds of brass; there is usually from 12 to 18 per cent. of zinc. Brass is very malleable and ductile when

* *Quarterly Journal of Science and the Arts*, vol. iv. p. 277.

† *Borate of Copper*. Solution of borax, poured into sulphate of copper, produces a bulky pale green precipitate of borate of copper.

Ferrocyanate of Copper is a brown compound, obtained by adding ferrocyanate of potassa to a dilute solution of sulphate or nitrate of copper. Mr Hatchett has recommended this substance as a brown pigment.

cold; and its colour and little liability to rust, recommend it in preference to copper for many purposes of the arts. According to M. Sage, a very beautiful brass may be made by mixing 50 grains of oxide of copper, 100 of calamine, 400 of black flux, and 30 of charcoal powder; melt these in a crucible till the blue flame is no longer seen round the cover; and, when cold, a button of brass is found at the bottom, of a golden colour, and weighing one-sixth more than the pure copper obtained from the above quantity of oxide.

1354. The analysis of brass may be performed by solution in nitric acid; add considerable excess of solution of potassa and boil, which will dissolve the oxide of zinc and leave that of copper; wash the latter, and dry and heat it to redness: 125 parts indicate 100 of copper. The zinc in the filtered alkaline solution may be precipitated by carbonate of soda, having previously added a small excess of muriatic acid; wash this precipitate, dry it, and expose it to a red heat; it is then oxide of zinc, 123 parts of which indicate 100 of metal.

Analysis of
brass.

1355. *Tutenag* is said to be an alloy of copper, zinc, and a little iron; and *Tombac*, *Dutch gold*, *Similor*, *Prince Rupert's metal*, and *Pinchbeck*, are alloys, containing more copper than exists in brass, and consequently made by fusing various proportions of copper with brass. According to Wiegleb, *Manheim gold* consists of 3 parts of copper and 1 of zinc. A little tin is sometimes added, which, though it may improve the colour, impairs the malleability of the alloy.*

Tutenag,
pinchbeck,
&c.

1356. *Bell-metal* and *bronze* are alloys of copper and tin; they are harder and more fusible, but less malleable than copper. The best bell-metal is composed of 80 parts copper and 20 of tin; the Indian gong, celebrated for the richness of its tones, contains copper and tin in this proportion. A little zinc is added to small shrill bells. Bronze consists of from 8 to 12 of tin with 100 of copper.

Bell-metal
and bronze.

1357. From a recent investigation, Mr Dalton finds that into all the alloys of copper which are characterized by useful properties, the ingredients enter in atomic proportions; and it is probable that by attention to these proportions, the manufacture of the artificial alloys may be greatly improved. H. 2. 111.

1358. The analysis of alloys of tin and copper may be performed by digestion in nitric acid, which dissolves the copper, and converts the tin into insoluble peroxide, which, when washed and dried, consists of 100 tin + 27 oxygen. The cupreous solution may be decomposed by potassa, and the pure peroxide of copper indicates the quantity of that metal, as in the analysis of brass. (1354.)

* An alloy, which, from the resemblance it has in colour to gold, is called *Mosaic gold*, has been lately prepared from equal parts of copper and zinc melted at the lowest temperature at which copper will fuse.

Speculum metal is an alloy of copper and tin, with a little arsenic; about 6 copper, 2 tin, 1 arsenic. On this subject the reader is referred to Mr Edwards's experiments. Nicholson's *Journal*, 4to. iii.

1359. Vessels of copper used for culinary purposes are usually coated with tin, to prevent the food being contaminated with copper. Their interior surface is first cleaned, then rubbed over with sal-ammoniac. The vessel is then heated, a little pitch or rosin spread over the surface, and a bit of tin rubbed over it, which instantly unites with and covers the copper.

Characteristics of the salts of copper.

1360. The cupreous salts are nearly all soluble in water, and of a blue or green colour. Ammonia produces a compound of very deep blue, when added in excess to these solutions, hydrosulphuret of ammonia forms a black precipitate; and a plate of iron plunged into a liquid salt of copper precipitates metallic copper.

Ferrocyanate of potassa is also an excellent test of the presence of copper; it produces a brown cloud in solutions containing the peroxide.* (1351, note.)

SECTION XVI. *Lead.*

To obtain pure lead.

1361. THE natural compounds of this metal are very numerous. The most important is the sulphuret, from which the pure metal is chiefly procured. Lead is also found combined with selenic, carbonic, sulphuric, phosphoric, arsenic, molybdic, and chromic acids, and with oxygen and chlorine. To obtain lead perfectly pure, Berzelius dissolved it in nitric acid, and crystallized the salt several times, till the mother liquor, on adding carbonate of ammonia, gave no traces of copper. The pure nitrate of lead, mixed with charcoal, was strongly heated in a Hessian crucible; and the lead, which separated, was kept for some time in fusion, in order to free it entirely from charcoal. The lead, thus obtained, when re-dissolved in nitric acid, gave no trace of any other metal.

Properties.

1362. Lead appears to have been known in the earliest ages of the world. Its colour is bluish white. It melts at 612° ,† and by the united action of heat and air is readily converted into an oxide, its specific gravity is 11.35. At common temperatures, it undergoes little change by mere exposure to air, but it is slowly corroded by the joint agency of air and water; hence the danger of leaden pipes and vessels for containing water which is intended to be drunk. Water appears also to act more readily on lead, when impregnated with the neutral salts that are occasionally present in spring water.‡ Exposed

* The oxidation of copper plates is a matter of very great importance in the arts, and in the case of great and expensive works where few impressions of an engraving are taken and the plates laid aside for a considerable length of time, a serious injury to the plate is sustained by the necessity of cleaning them from oxide, when they are to be again used. This may be prevented by varnishing the plates with common lac varnish, which can easily be removed, when requisite, by spirit of wine. Brewster's Jour. i. 76. Bost. Jour. ii. 206.

† Crichton.

‡ On the presence of lead in water, consult Dr Lamb's "Researches respecting Spring Water," (8vo. Lond. Johnson) and also Guyton, 26 Nich. Jour. 102.

upon ignited charcoal to a current of oxygen gas, it burns with a blue flame, throwing off dense yellow fumes of oxide. The alchemists gave this metal the name of *Saturn*.

1363. *Oxides of Lead.* There are three oxides of lead. Oxides.
The *protoxide* is the basis of the salts; it may be obtained pure by heating the nitrate of lead to redness in a vessel with a small orifice, till the whole of the acid is expelled. It is insipid and insoluble in water, of a pale yellow colour, and, when fused, crystallizes on cooling in irregular scales. It is volatile at a bright red heat. It is very soluble in solutions of potassa and soda; and when in fusion, it readily dissolves several of the earthy bodies and of the common metallic oxides. If it be considered as a protoxide, consisting of one proportional of lead and one of oxygen, then the number 104 (deduced from the mean of the best analysis) will represent lead, and it will consist of 104 lead + 8 oxygen. This oxide is known in commerce under the name of *massicot*; or when vitrified, as Massicot. obtained by calcining lead upon a large scale, it is called *litharge*.

When melted lead is exposed for some time to the air, it becomes incrustated with a grey pellicle, which, on removal, is succeeded by another, and so on until the whole is converted into a greenish grey powder, consisting of a mixture of the protoxide with metallic lead.

1364. If the protoxide be exposed to heat and oxygen, it gradually acquires a bright red colour, and is known under the name of *minium* or *red lead*. This, however, is an impure Deutoxide. substance, containing sulphate of lead, muriate of lead with excess of base, oxide of copper, silica, and a portion of the yellow oxide. The protoxide, Berzelius found, may be removed by acetic acid, which does not act on the red oxide, making allowance for the other impurities, he determined the composition of red oxide of lead, which may be considered as the deutoxide, to be lead 1 atom = 104 + $1\frac{1}{2}$ oxygen = 12. H. 2. 115.*

1365. The *peroxide* of lead may be obtained by the action of Peroxide. nitric acid on minium; but the most convenient method of preparing it is by transmitting a current of chlorine gas through a solution of acetate of lead. In this process water is decomposed, —its hydrogen uniting with chlorine, and its oxygen with the protoxide of lead, gives rise to muriatic acid and the peroxide of lead.

1366. The peroxide is of a flea or puce colour, very fine and light in its texture, and insoluble in nitric acid. When strongly heated it gives out 3 or 4 per cent. of oxygen gas, and is converted into yellow oxide.

* To succeed in obtaining it of a fine red tint, it requires to be manufactured in quantities, and with several precautions. The method employed in Derbyshire is described in Watson's *Chemical Essays*, vol. iii. p. 338.

It consists, according to Berzelius, of 1 atom lead + 2 atoms oxygen.

1367. The oxides of lead are easily vitrified, and have the property of uniting with all the metals except gold and silver. Hence gold or silver may be purified by melting them with lead. See (1376.)

Oils dissolve the oxide of lead, and become thick and consistent; in which state they are used as the basis of plasters, cements for water-works, paints, &c.

Action of
heat.

1368. The oxides of lead give up a part of their oxygen on the application of heat. When distilled in an earthen retort, they afford oxygen gas; and still more readily when distilled with concentrated sulphuric acid. They are completely reduced by being ignited with combustible matter. Thus when a mixture of red oxide of lead and charcoal is ignited in a crucible, a button of metallic lead will be found at the bottom of the vessel. Mere trituration of the peroxide in a mortar with a little sulphur, and the subsequent addition of a small bit of phosphorus, occasions a violent explosion.* H. 2. 117.

Chlorides.

Exp:

1369. *Lead and Chlorine.—Chloride of Lead.* When 30 grains of lead reduced to fine filings, are thrown into 60 cubic inches of chlorine gas, moderately warmed, the metal burns with a clear white flame accompanied with sparks.† The combination of lead and chlorine may, however, be more easily effected, by precipitating the nitrate or any soluble salt of lead with a solution of common salt, and washing the precipitate with a sufficient quantity of water.

The same substance is obtained by adding muriatic acid to nitrate of lead; it is white and fusible, and on cooling forms a hornlike substance (*plumbum corneum*.) It volatilizes at a high temperature. It dissolves in 22 parts of water at 60°; is more soluble in boiling water, separating, as the solution cools, in small acicular crystals, unchanged by exposure to air, and of a sweetish taste. It dissolves in dilute nitric acid. It has been analyzed by Berzelius, who states it to consist of 100 muriatic acid + 409,06 protoxide of lead, equivalent to 380,06 metallic lead = 129 chlorine. Dr J. Davy found it to be composed of

| | | | |
|--------------------|-----------------|-----------------|------|
| Chlorine | 25,78 | 34,75 | 36 |
| Lead | 74,22 | 100, | 104 |
| | 100, | | 140. |

1370. When two parts of the red oxide of lead are made into paste with one of muriate of soda, and water added occasionally as the mixture hardens, soda is disengaged, and a *subchloride* of lead is formed mixed with oxide of lead. This, on fusion, affords a fine yellow pigment called *mineral or patent yellow*. The disengaged soda attracts carbonic acid from the atmosphere,

Patent
yellow.

* Thomson's Ann. ix, 31.

† Or laminated lead may be heated in chlorine, which will be absorbed and chloride of lead will result.

but not enough to convert it into carbonate. In the large way, it is found necessary to supply carbonic acid to the soda thus formed, by burning it with saw-dust. By this process a large quantity of soda was extracted from common salt till cheaper methods were discovered. H. 2. 118. When treated by nitric acid, it forms nitrate of lead and a portion of chlorine separates.*

1371. *Nitrate of Lead* is obtained by dissolving the metal, Nitrate. not in excess, in dilute nitric acid, and evaporation. The salt crystallizes in tetraëdra and octoëdra, which are white, translucent, and of a styptic taste. It is soluble in 8 parts of water at 212° . It consists of 112 oxide of lead + 54 nitric acid. The alkalies throw down protoxide of lead from the solution of this salt.

1372. *Subnitrate of Lead* (*dinitrate* T.) may be formed by Subnitrate. boiling a mixture of equal weights of nitrate and protoxide of lead in water, filtering while hot, and setting it by to crystallize; it forms pearly crystals, of a sweet astringent taste.† It consists of two proportionals oxide = 224, + one proportional nitric acid = 54.

1373. Chevreul and Berzelius have described three *nitrites* of lead.‡ A detailed account of them is given by Dr Thomson.§

1374. *Hypo-nitrate of Lead*.—Berzelius obtained this salt Hypo-nitrate. by dissolving a given quantity of di-nitrite of lead in water, adding sufficient sulphuric acid to throw down half the lead, filtering the solution, and allowing it to crystallize spontaneously. The crystals consist of 1 atom hyponitrous acid, 1 protoxide of lead, and 1 of water. H. 2. 120.

1375. *Sulphuret of Lead* may be formed artificially by Sulphuret, fusion. Its lustre and colour much resemble pure lead, but it is brittle: it consists of 104 lead + 16 sulphur.

1376. *Native Sulphuret of Lead*, or *Galena*, is the principal Native. source of the vast commercial demands of the metal. It occurs massive and crystallized, particularly in limestone rocks. Its primitive form is the cube, of which there are several modifications, and among them the octoëdron. It often contains traces of silver, and sometimes in such quantity as to render it

* *Chlorate of Lead* is obtained by digesting the protoxide in chloric acid; it separates by slow evaporation, in white crystalline flakes of a very sweet taste. When heated it gives out oxygen and becomes a chloride.

• *Bromide of lead* was precipitated by Mr Balard from a solution of lead by hydrobromic acid. It is fusible by heat, and on cooling, concretes into a yellow mass. When first precipitated it was decomposable by nitric and sulphuric acid. When fused, boiling sulphuric acid was required to produce this effect. *Quart. Jour.* 44. 388.

• *Iodide of Lead*, formed by heating leaf lead with iodine, is a yellow insoluble compound. It is also formed by adding hydriodic acid or hydriodate of potassa to solution of nitrate of lead. It consists of 1 atom of iodine and 1 of lead.

• An insoluble *Iodate of Lead* is thrown down on adding iodate of potassa to any of the soluble salts of lead.

† Chevreul *Annales de Chimie*, lxxxii.

‡ *Ann. de Chim.* lxxxiii. and lxxxviii.

§ *System*, ii. 578.

Cupellation. worth separating, which is effected by exposing the roasted sulphuret to the action of heat and air in shallow earthen dishes; the lead becomes oxidized and converted into litharge, while the silver is left pure, in consequence of its power of resisting the influence of heat and air. This process is called *cupellation*. The litharge is afterwards reduced by fusion with charcoal.*

Reduction of galena. The reduction of galena upon a large scale is a sufficiently simple process. The picked ore, after having been broken and washed, is roasted in a reverberatory fire, the temperature being such as to soften but not fuse it. During this operation it is raked till the fumes of sulphur are dissipated, when it is brought into perfect fusion; the lead sinks to the bottom, and is run out into oblong moulds called *pigs*; the scorix are again melted, and furnish a portion of less pure metal.

The mines of Great Britain afford an annual produce of about 48000 tons of smelted lead, of which nearly the whole is obtained from the sulphuret.†

Sulphate. 1377. *Sulphate of Lead.* When metallic lead is boiled in concentrated sulphuric acid, sulphurous acid is evolved, and a white sulphate of lead is formed. It is so nearly insoluble, that it may be formed by adding dilute sulphuric acid, or an alkaline sulphate, to a solution of nitrate of lead. Dr Thomson found, that after having been dried at a temperature of 400° , it might be heated to redness in a platinum crucible without losing weight. Heated on charcoal by the blow-pipe, it is decomposed and reduced. It consists of one proportional of sulphuric acid = 40, and one proportional of oxide of lead = 112; and its representative number is therefore 152. Sulphate of lead is insoluble in alcohol and in nitric acid: it is sparingly soluble in dilute sulphuric acid, and separates from it in small prismatic crystals.

The insolubility of lead in sulphuric acid occasions its being employed as the material for constructing the chambers in which that acid is prepared, and even for boiling down the weak acid.

Tests of lead. 1378. All the solutions of lead are decomposed by sulphuretted hydrogen and by alkaline hydro-sulphurets, and a hydro-sulphuretted oxide is thrown down. Hence these compounds are excellent tests of the presence of lead in wine or any other

* The quantity of lead required for silver of various degrees of fineness may be learned from a memoir of D'Arcet in the first volume of *Annales de Chim. et de Phys.*

† *Hyposulphite of Lead* is precipitated in the form of a white powder, nearly insoluble in water, by adding solution of nitrate of lead to hyposulphite of potassa. It is composed, according to Herschel, of 70,30 protoxide of lead + 29,70 hyposulphurous acid. These numbers correspond to one proportional of oxide of lead = 112 + 2 proportionals of hyposulphurous acid = 48.

Sulphite of Lead may be obtained by digesting yellow oxide of lead in sulphurous acid; or by adding sulphurous acid or sulphite of potassa to nitrate of lead. It is white, insoluble, and tasteless, and consists of one proportional of each of its components; namely, 32 sulphurous acid + 112 oxide of lead. When heated it loses sulphurous acid.

liquor, discovering it by a dark coloured precipitate.* Hence, also, characters traced with solution of acetate of lead, become legible when exposed to sulphuretted hydrogen gas. The same property explains, too, the effect of alkaline hydro-sulphurets in blackening the glass bottles, in which they are kept. The effect is owing to the action of sulphuretted hydrogen on the oxide of lead, which all the white glass contains.†

1379. *Phosphate of Lead* is formed by mixing solutions of nitrate of lead and phosphate of soda, or phosphoric acid. It is yellowish white; insoluble in water; soluble in alkaline solutions, and in nitric acid. It is decomposed by sulphuric acid, and by hot muriatic acid. It fuses before the blow-pipe, and crystallizes on cooling. It consists of 112 oxide of lead + 28 phosphoric acid = 140.‡

Phosphate.

1380. *Carbonate of Lead*.—When an alkaline carbonate is added to nitrate of lead, a white precipitate of carbonate of lead falls: it is tasteless, insoluble in water, but soluble in fixed alkaline solutions. It is employed as a white paint, under the name of *white lead* or *ceruse*, and is usually prepared by exposing sheet lead to the action of the vapour of vinegar.§ It consists of 112 oxide of lead + 22 carbonic acid = 134 carbonate of lead.||

Carbonate.

1381. The soluble salts of lead have a sweetish austere taste, and are characterized by the white precipitate produced by ferrocyanate of potassa, the deep brown by hydro-sulphuret of ammonia, and the yellow by hydriodate of potassa.

Characters of the salts of lead.

1382. The salts insoluble in water are dissolved by soda and potassa, and by nitric acid, when the metal is rendered manifest by sulphuretted hydrogen and other tests. Heated by the blow-pipe upon charcoal they afford a button of metal.

1383. *The Alloys of Lead* with the metals described are not important, if we except that which it forms with tin. Common *pewter* consists of about 80 parts of tin and 20 of lead. Equal parts of lead and tin constitute *plumber's solder*; and what is termed *pot-metal* is an alloy of lead and copper.

Alloys.

1384. In analyzing these alloys, 100 grains in filings may be boiled to dryness in two ounces of nitric acid, water poured upon the residue, and filtered; the peroxide of tin remains on the filter, and the nitrate of lead, which passes through in solution, may be converted into sulphate by adding sulphate of soda.

Analysis of.

* Or, subcarbonate of ammonia, which is a very delicate test, may be employed to precipitate the lead in a state of white carbonate, which, on being washed and digested with sulphuretted hydrogen water, will instantly become black. U.

† *Phosphuret of Lead* may be formed by dropping phosphorus into melted lead. It is of the colour of lead, and soon tarnishes. *Phosphite of Lead* was prepared by Berzelius by mixing muriate of lead with phosphite of ammonia. It is white, tasteless, and insoluble, and appears to consist of 1 proportional of oxide of lead + 1 proportional of phosphorous acid.

‡ *Ann Philos.* 1. 12.

§ The process is described in Aikin's *Dictionary*, (Art. Lead.)

|| *Borate of Lead* is precipitated in the form of a white powder, when borate of soda is mixed with nitrate of lead. Lead occurs combined with selenium. See *Boston Jour.* ii. 597.

152 grains of sulphate of lead dried at a red heat, indicate 104 of metal; and 75 grains of washed peroxide of tin are equivalent to 59 grains of metallic tin.

1385. With potassium lead forms a brittle and very fusible alloy; with sodium the compound is equally brittle but less fusible. When exposed to air these alloys suffer decomposition in consequence of the oxidizement of the alkaline bases. The alloy of lead and manganese has not been examined. When lead is fused with iron, two alloys are obtained; that at the bottom of the crucible consisting of lead with a little iron, while the superficial portion is iron with a little lead.* With zinc, lead forms a hard ductile alloy.

Eliquesation.

1386. If lead be heated so as to boil and smoke, it soon dissolves pieces of copper thrown into it; the mixture, when cold, is brittle. The union of these two metals is remarkably slight; for upon exposing the mass to a heat no greater than that in which lead melts, the lead almost entirely runs off by itself. This process is called *eliquesation*. The coarser sorts of lead, which owe their brittleness and granulated texture to an admixture of copper, throw it up to the surface on being melted by a small heat. U. 544.

SECTION XVII. Antimony.

Ores.

1387. This metal is found *native* in Sweden, in France, and in the Hartz; but its principal ore is the *sulphuret* which is found massive and crystallized, and of which there are several varieties. The most common is the *radiated*, which is of a grey colour and brittle. This ore may be decomposed, and the pure metal obtained from it, by the following process:

Reduction of.

Mix three parts of the powdered sulphuret with two of crude tartar, and throw the mixture by spoonfuls into a red-hot crucible; then heat the mass to redness, and a button will be found at the bottom of the crucible, which is the metal as it commonly occurs in commerce, and is nearly pure. Reduce this button to fine powder, and dissolve it in nitro-muriatic acid, pour this solution into water, which will occasion the precipitation of a white powder, which is to be washed and mixed with twice its weight of tartar and exposed to a dull red heat in a crucible. The button now obtained is pure antimony.

Or, two parts of the sulphuret may be fused in a covered crucible with one of iron filings, and to these when in fusion, half a part of nitre may be added. The sulphur quits the antimony and combines with the iron.

Properties.

1388. Antimony (sometimes called *regulus of antimony*.) is of a silvery white colour, brittle, and crystalline in its ordinary texture. It fuses at about 810° and is volatile at a high heat. Its specific gravity is 6,70† (6,424 T.) Placed upon

* Guyton Morveau, *Ann. de Chim.* lvii.

† Hatchett, *Philos. Trans.* 1803.

ignited charcoal, under a current of oxygen gas, antimony burns with great brilliancy, throwing off its oxide in the form of a dense yellow smoke.

The vapour of water, brought into contact with ignited antimony, is decomposed with so much rapidity as to produce a series of detonations. H. 2. 72. Decomposes water.

1389. *Antimony and Oxygen*.—Considerable differences exist among chemists, as to the composition of the oxides of antimony. Thenard* maintains the existence of six oxides, Proust† of two, Berzelius‡ of four, and Thomson§ of three. Oxides.

The opinion of Dr Thomson is now admitted by most chemists; and there is reason to believe that the proportions which he has assigned to these oxides are very near the truth.

| | Antimony. | | Oxygen. | |
|-----------------|-----------|-----------|---------|------|
| Protoxide . . . | 44 | or 1 atom | — 8 | = 52 |
| Deutoxide . . . | 44 | " 1 | " — 12 | = 56 |
| Peroxide . . . | 44 | " 1 | " — 16 | = 60 |

1390. *Protoxide of Antimony* is thus obtained: To 200 parts of sulphuric acid add 50 parts of powdered metallic antimony. Boil the mixture to dryness, wash the dry mass, first in water, and then with a weak solution of carbonate of potassa; a white powder remains, which when thoroughly washed with hot water, is protoxide of antimony. It may also be procured by dissolving the sulphuret of antimony in muriatic acid, pouring the solution into water, and washing the white precipitate with weak solution of potassa. Protoxide.

1391. This oxide may also be obtained by adding ammonia to solution of tartrate of antimony and potassa, heating the mixture and washing the precipitate in large quantities of boiling water. It is thus procured in the form of a heavy white powder.

This protoxide exists in all the active antimonial preparations; in emetic tartar, kermes, glass of antimony, golden sulphuret, &c. It is fusible and volatile at a red heat: decomposed by sulphur and charcoal, and when acted on by nitric acid, is converted into peroxide. If heated with chlorate of potassa it deflagrates and also becomes peroxidized; it is very soluble in muriatic acid, and readily forms emetic tartar when boiled in solution of tartrate of potassa.

1392. The presence of antimony in solution is easily detected by sulphuretted hydrogen. This gas occasions an orange Test.

* *Ann. de Chim.* xxxii. † *Jour. de Phys.* lv.
‡ *Ann. de Chim.* lxxxiii, and *Ann. de Chim. et Phys.* xvii. § *First Prin.* ii.
|| Dr Thomson was led by his experiments to assign to these oxides the following proportions:

| | | | | | |
|-----------|-------|-----|-------|--------|--------|
| Protoxide | - - - | 100 | metal | + 18,2 | Oxygen |
| Deutoxide | - - - | 100 | " | + 27,3 | " |
| Peroxide | - - - | 100 | " | + 36,4 | " |

These proportions are more consistent with the general law of chemical combination, than the results of Berzelius; though they present, with respect to the deutoxide, the same anomaly as in the case of one or two other metals, viz., that the multiple of the oxygen of the first oxide is $1\frac{1}{2}$ and not an entire number.

coloured precipitate, the hydrated protosulphuret of antimony, which is soluble in pure potassa, and is dissolved with disengagement of sulphuretted hydrogen by hot muriatic acid, forming a solution from which the white submuriate is precipitated by water. T. 409.

Deutoxide.

1393. *Deutoxide*.—When antimony burns, or is strongly heated in open vessels, the deutoxide is generated, sublimes, and condenses on cold surfaces in the form of acicular crystals of silvery whiteness, formerly called *argentine flowers of antimony*.

This oxide does not fuse readily, but is more volatile than the protoxide. It is quite insoluble in water, and in the anhydrous state is attacked with great difficulty by acids. It combines with alkalis, and for this reason it has been called *antimonious acid*, and its salts *antimonites*, by Berzelius.

The antimonious acid is precipitated from these salts by acids as a hydrate, which reddens litmus paper, and is dissolved by muriatic acid, though without appearing to form a definite compound.

Peroxide,
how obtain-
ed.

1394. *Peroxide of Antimony* or *Antimonic Acid*, is procured by acting for a considerable time upon the powdered metal, by excess of hot nitric acid, and exposing the product to a red heat, to expel the redundant acid.*

Another pro-
cess.

It is also formed by exposing the metal or the protoxide mixed with five or six parts of nitre to a red heat in a porcelain crucible, and washing the residue with hot water.† It is yellowish white; but becomes buff-coloured when heated, and returns to its former tint on cooling. It neither fuses nor volatilizes at a bright red heat, but when exposed to the flame of a spirit-lamp urged by a blow-pipe, it passes off slowly in white fumes, being partially reduced by the hydrogen of the flame.

Chlorides.

1395. *Antimony and Chlorine*.—When antimony in powder is thrown into a jar of chlorine gas, it takes fire and the *proto-chloride* of antimony is formed. It may also be produced by the distillation of one part of powdered antimony with two and a half of bi-chloride of mercury (corrosive sublimate.) This chloride is a soft solid at common temperatures, but becomes liquid by a gentle heat, and crystallizes as it cools. It is the *butter of antimony* of old writers. It deliquesces by exposure to air; and is a powerful caustic. When water is added to it a precipitate falls, formerly called *Algarotti's powder*, or *mercurius vitæ*, which is a submuriate of the protoxide.

The chloride of antimony consists of one atom of each constituent.

1396. The *bi-chloride* is generated by passing dry chlorine gas over heated metallic antimony. It is a transparent volatile liquid, which emits fumes on exposure to the air, mixed with

* The *diaphoretic antimony* and *Bezoar mineral* of old Pharmacopœiæ, consisted of this oxide, which, compared with the protoxide, is nearly inert.

† Or by projecting powdered metallic antimony into red-hot nitre. H.

water it is converted into muriatic acid and the hydrated peroxide, which subsides. It contains twice as much chlorine as the proto-chloride.*

1397. Dr Thomsont has described another chloride of antimony, composed of 1 atom of chlorine and 2 atoms of the metal. It is, therefore, a *dichloride*.†

1398. Nitric acid acts powerfully on metallic antimony, and if mixed with it in fine powder, will sometimes cause its inflammation. The metal becomes peroxidized, and scarcely an appreciable portion is retained in solution. As in some other cases of the vehement decomposition of nitric acid, ammonia is produced, which may be rendered sensible by pouring potassa on the white magma that results.

Action of nitric acid,

1399. Nitro-muriatic acid readily dissolves antimony, and forms an orange-coloured solution, which is decomposed by the addition of water. Iron or zinc immersed in this solution throws down a black powder, which, according to Thenard, is pyrophoric.

— of nitro-muriatic.

1400. *Sulphuret of Antimony* is easily formed by fusing the metal with sulphur. This artificial sulphuret, exactly resembles the native compound, which last may be employed on account of its cheapness, for exhibiting the properties of sulphuret of antimony. The proportions of its ingredients, as stated by Berzelius, differ from those assigned by Proust, viz.

Sulphuret.

| | | | | | |
|------------------|-------|---------|-------|---------|-----|
| Antimony | 72,86 | | 100, | | 270 |
| Sulphur | 27,14 | | 37,25 | | 100 |

100.

Dr Thomson makes it to consist of 44 metal + 16 sulphur, or of 100 metal + 36 sulphur. H. 2. 77.

1401. When the native sulphuret (*crude antimony*) is exposed under a muffle to a dull red heat, it gradually loses sulphur and absorbs oxygen, being converted into a grey powder, which consists of a mixture of protoxide of antimony and sulphuret. If the heat be increased, this fuses into a transparent substance of a yellow or brown colour, formerly called *glass of antimony*. Its composition is variable; it generally contains about 85 *per cent.* of protoxide and 15 of sulphuret. In that which is imported for pharmaceutical purposes, from Germany and Holland, there is usually a portion of siliceous earth. and it is sometimes adulterated with the oxide of lead. This fraud is easily detected by digesting the finely powdered glass in hot nitric acid, diluting the solution and filtering. The filtered liquor gives a white precipitate on the addition of sulphate of soda if lead were present.

Glass of antimony.

During the formation of glass of antimony, if the heat be raised too high the greater part of the protoxide sublimes in

* Rose, in *Ann. Philos. N. S.* x.

† *First Prin.*

‡ *Iodide of Antimony* is of a dark red colour; acted upon by water, it produces hydriodic acid and oxide of antimony.

slender crystalline needles; while another portion, if air be not excluded, passes into the state of peroxide, and undergoes no change at a very high temperature.

Crocus metallicum.

1402. Eight parts of oxide and two of sulphuret give an opaque compound, of a red colour inclining to yellow; and called *Crocus metallorum*. With eight parts of oxide and four of sulphur, we obtain an opaque mass of a dark red colour, called *liver of antimony*.* H.

Kermes mineral.

1403. When sulphuret of antimony is boiled in a solution of potassa, a liquid is obtained, from which as it cools, an orange coloured matter, called *kermes mineral*, is deposited; and on subsequently neutralizing the cold solution with an acid, an additional quantity of a similar substance, the *Golden Sulphurett* subsides.

1404. The *Sesqui-sulphuret* of antimony is obtained by passing sulphuretted hydrogen through a solution of the deutoxide, in dilute muriatic acid †

1405. M. Rose formed the *bisulphuret*, consisting of 1 atom of antimony and 2 atoms of sulphur, by the action of sulphuretted hydrogen on a solution of the peroxide.

1406. M. Rose has also demonstrated that the *red antimony* of mineralogists is a compound of 1 atom of the protoxide combined with 2 atoms of the proto-sulphuret of antimony. The pharmaceutic preparations known by the terms *glass*, *liver*, and *crocus* of antimony, are of a similar nature, though less definite in composition, owing to the mode by which they are prepared.

Antimoniates.

1407. When the sulphuret of antimony is detonated with twice its weight, or upwards, of powdered nitre, the sulphur is oxygenated by the oxygen of the nitric acid; sulphate of potassa is formed, and an oxide of antimony is obtained, varying in its degree of oxidation, with the proportion of nitre which has been employed. The oxide remains, after washing away the sulphate with boiling water. If four times its weight of nitre be employed, the metal gains 33 per cent. of oxygen; acquires the characters of an acid; and forms, with potassa, a crystallizable compound, or *antimoniate*. H. 2. 78. §

Phosphate.

1408. *Phosphate of Antimony* has not been formed: in the *Ū S. Pharmacopœia* there is a preparation called *pulvis antimonialis*, formed by heating one part of sulphuret of antimony with two of hartshorn shavings. The action of heat upon the sulphuret has already been described. (1401.) Its effect upon the hartshorn shavings is to destroy the animal matter, leaving little else than phosphate of lime. So that the *pulvis antimo-*

* *Sulphate of Antimony*.—When sulphuric acid is boiled upon finely-powdered antimony, the metal is oxidized, and an acid sulphate and subsulphate of antimony are the results. In both these salts the metal is in the state of protoxide.

† *Antimonii sulphuretum precipitatum*. U. S. P.

‡ Rose, in *Ann. Philos.* N. S. x.

§ *Phosphuret of Antimony* is formed by heating together equal parts of oxide of Antimony, phosphoric acid, and charcoal. It is white and brittle.

nialis consists essentially of protoxide of antimony, mixed with phosphate of lime. This preparation is usually considered analogous to, if not identical with, *James' Powder*, which, according to Dr Pearson's analysis,* consists of 43 phosphate of lime, and 56 oxide of antimony.†

James' powder.

1409. In examining Antimonial Powder from various sources, prepared according to the directions of the *Pharmacopœia*, Mr Brande has found it of very variable composition. For medical use, one of the best modes of preparing it would be to dissolve certain proportions of protoxide of antimony and phosphate of lime in muriatic acid, precipitate by ammonia, and edulcorate with a large quantity of water. Mr Chenevix advises for this purpose equal parts of the oxide and phosphate, but such proportion of antimony is too great: Mr Brande has made a useful Antimonial Powder by dissolving 200 grains of bone-earth and 100 of protoxide of antimony in a measured ounce and a half of muriatic acid, and pouring the solution into a weak solution of ammonia; the precipitate, when washed, dried, and reduced to a fine powder, weighed 280 grains.‡

Mr Brande's experiments on.

Mode of preparing antimonial powder.

1410. The solutions of antimony afford orange-coloured precipitates with sulphuretted hydrogen, and those which are acid are precipitated when largely diluted with water.

1411. Antimony forms brittle alloys with the malleable metals. When gold was alloyed with $\frac{1}{1920}$ its weight of antimony, the compound was perfectly brittle; and even the fumes of antimony in the vicinity of melted gold are sufficient to destroy its ductility.§ With potassium and sodium it forms white brittle compounds, destructible by the action of air and water.

Alloys.

Its alloys with manganese and with zinc have not been examined.

Alloyed with lead in the proportion of 1 to 16, and a small addition of copper, antimony forms the alloy used for *printers' types*. With lead only, a white and rather brittle compound is formed, used for the plates upon which music is engraved. With iron it forms a hard whitish alloy, formerly called *martial regulus*, which may be obtained by fusing two parts of sulphuret of antimony with one of iron filings; a scoria consisting

Type metal.

* *Phil. Trans.* 1791.

† Different formulæ have been given for imitating *James' Powder*, the real receipt having been studiously concealed and a false one published in its stead; that of Dr Pearson furnishes a mere mixture of oxide of antimony with phosphate of lime. Dr Ure has given a copy of the original specification lodged in Chancery. See *Ure's Dictionary*, p. 175.

‡ The following method furnishes, in the dry way, a tolerably uniform Antimonial powder: Burn two pounds of hartshorn to a cinder, reduce it to powder, and heat it to a dull redness in an iron pot; then gradually stir into it one pound of powdered sulphuret of antimony, added in successive portions, and continue the same heat as long as fumes arise; when these cease the mixture will have a dirty grey colour, and during the operation small crystals of protoxide of antimony will be seen to collect upon its surface when a portion is taken out in an iron spoon. In this grey state it should be put into a crucible and heated to intense redness; a phosphorescent light of a greenish tint is soon perceived, and when this ceases the crucible may be removed from the fire, and its contents when cold reduced to a fine powder, which should be perfectly white.

§ Hatchett. *Phil. Trans.* 1803.

chiefly of sulphuret of iron is formed, and the fused alloy beneath usually presents a stellated appearance in consequence of its crystallization. This star was much admired by the alchemists, who considered it a mysterious guide to transmutation. With tin, antimony constitutes a kind of *pewter*, a term, however, which has also been applied to some other alloys, especially that of lead and tin. The finest pewter consists of about 12 parts of tin and 1 of antimony, with a small addition of copper. A good white metal, used for teapots, is composed of 100 tin, 8 antimony, 2 bismuth, and 2 copper.*

SECTION XVIII. *Bismuth.*

Native.

1412. This metal is found native; combined with oxygen; and with arsenic and sulphur. *Native Bismuth* occurs crystallized in octoëdra and cubes, and in addition to arsenic generally contains cobalt.

Properties.

1413. Bismuth has a reddish white colour, and is composed of broad brilliant plates adhering to each other. Its specific gravity is 9,822, but is increased by hammering. It breaks, however, under the hammer, and hence cannot be considered as malleable; nor can it be drawn out into wire. The bismuth of commerce is not quite pure. To purify it, Dr Thomson dissolved it in nitric acid, decomposed the nitrate by water, edulcorated the oxide, and reduced it to a metallic state by heating it in a covered crucible with black flux.†

1414. Bismuth is one of the most fusible metals, melting at 476° Fahrenheit; and it forms more readily than most other metals, distinct crystals by slow cooling.

* The analysis of an alloy of tin, lead, copper, and antimony, may be thus performed: introduce 100 grains into a matrice with a wide mouth, and pour upon it one ounce of water and 2 of nitric acid; digest and evaporate to dryness. The dry mass will consist of the nitrates of lead and copper, which are soluble, and may be taken up by two ounces of hot water, and of the peroxides of tin and antimony, which are insoluble, and remain upon the filter.

To the solution of the nitrates add sulphate of soda, which throws down sulphate of lead, and which is to be collected in a filter, washed, dried at a red heat, and weighed. (1259.) The filtered liquor may be evaporated to about two ounces in bulk, and having rendered it slightly acid by dilute sulphuric acid, immerse in it a plate of iron, which will throw down metallic copper, to be purified if requisite, (1259,) dried and weighed.

The separation of the peroxides of tin and antimony is attended with many difficulties; it may be imperfectly effected by solution in nitro-muriatic acid, and subsequent dilution with a large quantity of water, which throws down the antimonial oxide, not however pure, but with a portion of peroxide of tin: the latter, retaining a little peroxide of antimony, may be procured by evaporation and exposure of the residue to a dull red heat in a porcelain cup.

In analyzing compounds of tin and antimony, it is necessary first to make an alloy, in which the antimony shall not exceed the proportion of $\frac{1}{20}$ th part, for then, concentrated muriatic acid, by digestion with this alloy, dissolves the tin, and leaves the antimony untouched; but if more than $\frac{1}{20}$ th part of antimony enters into the combination, the tin acquires the insolubility of that metal in muriatic acid. H. 2. 74. For a valuable paper, by Dr Turner, on the detection of antimony in mixed fluids, see Brewster's *Jour.* xv.

† Ann. of Phil. N. S. ii. 122.

It may be obtained in regular crystals, by fusing a quantity of it in a crucible, and allowing it to cool till a crust is formed on the surface, the extremity of the crucible may then be broken off, and the fluid metal beneath be allowed to escape. The under surface of the crust will be found beautifully crystallized.

Process for obtaining crystals.

1415. When bismuth is exposed to heat and air it oxidizes, forming a fusible *white oxide*. If the heat be increased by directing a current of oxygen upon the metal, it burns with much brilliancy, and produces an abundant yellow smoke, which condenses in the form of a yellowish white sublimate. When in fusion this oxide acts upon other oxides much in the same way as oxide of lead. According to the experiments of Dr J. Davy* it is composed of 72 parts of bismuth and 8 oxygen, and 72 is the atomic weight of the metal, and 80 of its oxide. This result is confirmed by the researches of Dr Thomson.† This oxide occurs, though very rarely, *native*: it has been found in Cornwall and Saxony. H.

Oxide.

1416. *Chloride of Bismuth* is procured by heating the metal in the gas, or by evaporating the muriate to dryness, and submitting the residue to distillation, when the chloride sublimes, and afterwards deliquesces into what was called *butter of bismuth*. A similar product is obtained by introducing finely divided bismuth into chlorine gas, when the metal takes fire and burns with a pale blue light. This compound is the only known *chloride of bismuth*.

Chloride.

Exp.

1417. It was analyzed by Dr Davy, and found to contain

| | | | | |
|----------|-------------|-------|-------------|------|
| Bismuth | : | 66,4 | : | 00 |
| Chlorine | : | 33,6 | : | 50,6 |
| | | <hr/> | | |
| | | 100. | | |

From this analysis, the equivalent of bismuth, also, appears very nearly to agree with the number derived from the sythe-sis† of the oxide. H.

1418. *Nitrate of Bismuth*.—Nitric acid dissolves bismuth with great rapidity. To one part and a half of nitric acid, add, at distant intervals, one of bismuth, broken into small pieces. The solution is crystallizable in small four-sided prisms.

Nitrate.

1419. The nitrate of bismuth consists of 1 proportion of oxide, + 1 of acid, and 3 of water.

1420. Nitrate of Bismuth is decomposed by water, and the oxide of bismuth is thrown down in the form of a fine white powder, called *magistery of Bismuth*, *pearl white*, or *blanc de fard*. In this state it has been used in medicine as a tonic.§

Pearl white.

* Phil. Trans. 1812.
† First Prin. vol. i.
‡ Iodide of Bismuth, obtained by heating iodine with the metal, is of an orange-colour, and insoluble in water. When hydrjodic acid or hydriodate of potassa is added to nitrate of bismuth, a precipitate falls of a deep chocolate-brown colour, insoluble in water but soluble in liquid potassa.
§ Quarterly Journal, iii, 295. If a small portion of muriatic acid be mixed with the nitric, and the precipitated oxide be washed with but a small quantity of cold water, it will appear in minute scales, constituting the *pearl-powder* of perfumers. These paints are liable to be turned black by sulphuretted hydrogen.
According to Mr R. Phillips a solution of bismuth, so dilute or so acid that water occasions no precipitate in it, is decomposed by the addition of common salt or muriatic acid. See Ann. of Philos. N. S. iii. 231.

Exp.

1421. If characters be written on paper with nitrate of bismuth they are invisible when dry, but become white and legible on immersion in water, thus forming a *white sympathetic ink*. The same characters are rendered brown or black by solution of sulphuretted hydrogen.

Sulphuret.

1422. *Sulphuret of Bismuth*.—Bismuth combines with sulphur, and forms a bluish grey sulphuret, having a metallic lustre, which is also found native. The primitive form of its crystals is a right rhombic prism.* Lagerhjelm has analyzed it, and found it to consist of

| | | | | | | |
|---------|---------|--------|---------|-------|---------|--------------|
| Bismuth | | 86,191 | | 100 | | 71 |
| Sulphur | | 18,331 | | 22,52 | | 16 |
| | | <hr/> | | | | <hr/> |
| | | 100. | | | | 37† H. 2.96‡ |

Sulphate.

1423. *Sulphate of Bismuth*.—Sulphuric acid acts when hot and concentrated, on bismuth, and sulphurous acid is disengaged. A part of the bismuth is dissolved; and the remainder is changed into an insoluble oxide. It consists of one proportional oxide and one acid. It is a white compound, insoluble in, but decomposed by water, which converts it into a *subsulphate* and *supersulphate*. The subsulphate described by Berzelius consists of three proportionals of oxide and one acid.§

Alloys.

1424. Bismuth forms *alloys*, some of which are remarkable for their fusibility. With gold, platinum, and silver, it forms brittle compounds. A compound of eight parts of bismuth, five of lead, and three of tin, liquefies at 212° ; it is called Sir I. Newton's *fusible metal*.|| The addition of one part of quicksilver renders it yet more fusible. Bismuth enters into the composition of *soft solders*. These alloys are mostly white, brittle, and easily oxidated.¶

* Phillips, in *Ann. Philos.* N. S. ii. 181.

† The compound analyzed by Vanquelin appears to have been a *bi-sulphuret*. *Annales du Muséum*. Tom xv.

‡ Dr Thomson found that 9 grains of pure bismuth converted into a sulphuret became 11 grs.; hence the sulphuret is composed of

| | | | | | | |
|---------|-------|-------|-------|-----------|-------|-------|
| Bismuth | - - - | 81,82 | - - - | or 1 atom | - - - | 72 |
| Sulphur | - - - | 18,18 | - - - | " " | - - - | 16 |
| | | <hr/> | | | | <hr/> |
| | | 100. | | | | 88 |

§ *Hydrosulphuretted Oxide of Bismuth* is of deep brown approaching to black. It is thrown down from nitrate of bismuth by sulphuretted hydrogen.

|| The alloy composed of lead 340 parts, tin 194 parts, and bismuth 466 parts, according to Dübeneiner, is fusible at 210° F. It may be considered as composed of 1 atom of an alloy of bismuth and lead, fusible at $323^{\circ},6$ or $336^{\circ},2$ F. united to 1 atom of an alloy of bismuth and tin, which fuses at $267^{\circ},8$, or $278^{\circ},6$, F. When the combination of these alloys takes place, it produces cold. On mixing 207 parts of lead, 118 of tin, 284 of bismuth, and 16,17 of mercury at the temperature of $63^{\circ},5$ F. the thermometer instantly descended to 14° F. *Ann. de Chim.* xxxvi. 334.

¶ An alloy of bismuth and lead may be analyzed by dissolving in dilute nitric acid, pouring into the solution one of carbonate of ammonia, which at first precipitates both oxides in the state of carbonate; and when added in excess, re-dissolves the carbonate of bismuth. The carbonate of lead is to be washed in the filter with solution of carbonate of ammonia, in order to dissolve any adhering carbonate of bismuth: the washing is to be finished with warm water, in order to dissolve all the carbonate of ammonia used in the washing. The alkaline liquor containing the oxide of bismuth, is to be saturated by an acid, and then ammonia is to be added in excess; all the oxide of bismuth, is precipitated, and after washing on a filter is to be dried. M. Laugier, in *Ann. de Chim.* xxxvi. 333.

Analysis of
Alloy of bis-
muth and
lead.

Bismuth has the singular property of depriving gold of its ductility; even when combined with it in very minute proportion. This effect is produced by merely keeping gold in fusion near melted bismuth. It has, nevertheless, been employed by Chaudet in cupellation.* H. 2. 97.

SECTION XIX. Cobalt.

1425. THE native combinations of cobalt are the oxide, and compounds of the metal with iron, nickel, arsenic, and sulphur. Ores. It is also found combined with arsenic acid. According to Stromeyer it is a constant ingredient of meteoric iron. In the white and grey cobalt ores, the metal is combined with iron, and with arsenic: some of the varieties are crystallized in cubes, octoëdrons and dodecaëdrons. The red ore is an arseniate. The finest specimens are the produce of Saxony.

1426. To obtain pure cobalt, the cobalt of commerce, in fine powder, may be calcined with four parts of nitre, and washed in hot water, by which arsenic is separated:† then digest in dilute nitric acid, and immerse a plate of iron, which will separate the copper; filter and evaporate to dryness; digest the dry mass in liquid ammonia and filter, expel the excess of ammonia from the filtered liquor by heat, taking care not to produce a precipitate, and then add solution of potassa, which throws down oxide of nickel; filter immediately, and boil, which will occasion the separation of oxide of cobalt, and which, ignited with charcoal, furnishes the pure metal. In this process the first calcination with nitre often requires two or three repetitions in order to get rid of the whole of the arsenic, which adheres to cobalt with much obstinacy.‡ To obtain pure cobalt.

1427. Metallic cobalt may also be obtained by dissolving zaffre in muriatic acid, and transmitting through the solution a current of sulphuretted hydrogen gas, until the arsenious acid is completely separated in the form of sulphuret of arsenic. The filtered liquid is then boiled with a little nitric acid, in order to convert the protoxide into the peroxide of iron, and an excess of the carbonate of potassa is added. The precipitate, consisting of the peroxide of iron and carbonate of cobalt, after being well washed with water, is digested in a solution of oxalic acid, which dissolves the iron, and leaves the cobalt in the form of an insoluble oxalate.§ On heating the oxalate of cobalt in a retort from which the atmospheric air is excluded, a large quantity of carbonic acid is evolved and a black powder, metallic cobalt, is

* *Ann. de Chim. et Phys.* vi. 113.

† According to M. Boullay pulverized arsenical cobalt ore, in large quantity, is liable to spontaneous combustion. *Quar. Jour.* N. S. iv.

‡ For M. Woehler's method of separating arsenic from cobalt see *Quar. Jour.* N. S. iii. 209.

§ *Laugier.*

left.* The pure metal is easily procured also by passing a current of dry hydrogen gas over the oxide of cobalt heated to redness in a tube of porcelain. T. 416.

Properties.

1428. Cobalt has a greyish white colour, inclining to pink; its specific gravity is 8; it is brittle and easily reduced to powder, but is very difficultly fusible. When slowly cooled after fusion it may be obtained in irregular prisms. It is magnetic and was found by Wenzel to be convertible into a magnet, having all the properties of the magnetic needle.

Protoxide.

1429. By exposure to the atmosphere cobalt is tarnished, but not oxidized to any extent. In an intense heat it burns with a red flame; but, if pure, it is not easily oxidized by a moderate temperature. Its oxide, formed by long exposure to a strong heat with access of air, is of a deep blue, approaching to black. This, from the experiments of Thenard, appears to be the *protoxide*, which may be obtained, also, by precipitating the nitrate of cobalt with potassa. The precipitate, which at first is a bright blue hydrate, becomes when dry of so dark a blue as to appear black. It dissolves readily in muriatic acid, giving a solution which is green when concentrated, and red when diluted. Its solutions in sulphuric and nitric acids are always red. H. 2. 87.

1430. By exposure to heat and air the protoxide absorbs an additional portion of oxygen and is converted into black *peroxide*. All the salts of cobalt contain the protoxide.

Peroxide.

1431. The black or *peroxide*, heated for half an hour at the bottom of a crucible, loses a part of its oxygen, and is reduced to the state of protoxide. The protoxide is composed,

| | Metal | Oxygen | Metal | Oxygen |
|-------------------------|-------------|-------------|-----------|--------|
| According to Proust, of | 83,5 . . . | 16,5 . . . | 100 . . . | 19,3 |
| ———— Rolhoff, | 79,56 . . . | 21,44 . . . | 100 . . . | 27,3 |
| ———— Thomson, | | | 100 . . . | 28,5 |
| ———— Brande, | | | 100 . . . | 24,7 |

And peroxide of cobalt consists,

| | Metal | Oxygen | Metal | Oxygen |
|-------------------------|----------|----------|-----------|--------|
| According to Proust, of | 75 . . . | 25 . . . | 100 . . . | 33,25 |
| ———— Rolhoff, | 71 . . . | 29 . . . | 100 . . . | 40,85 |

Rolhoff ascertained that 100 parts of peroxide of cobalt, exposed to a strong heat, lose from 9,5 to 9,9† Taking the mean 9,7, we have 100 of the peroxide composed of 9,7 oxygen + 90,3 protoxide, the oxygen in which, according to the same authority, is 19,3. Therefore $9,7 + 19,3 = 29$, is the oxygen in 100 of the peroxide; or 100 of the metal condense 40,85 oxygen. Hence the protoxide contains $1\frac{1}{2}$ times as much oxygen as the protoxide. For $27,3 + 1\frac{1}{2} = 40,95$ very nearly. If then the protoxide consists of 1 atom metal + 1 of oxygen, the equivalent number for cobalt will be 30 (strictly 29,304); for the protoxide, 38, and for the peroxide 42. H. 2. 88.

Chloride.

1432. Cobalt burns when heated in chlorine; and forms *chloride of cobalt*. Mr Brande from the analysis of the chloride infers that 100 of chlorine unite with 91,1 of cobalt; but this would give for the equivalent of that metal a higher number 32,54 than that deducible from the composition of the oxide. H.

* Thomson, in *Ann. of Phil.* N. S. i.

† *Ann. Phil.* iii. 356.

1433. *Muriate of Cobalt* is a deliquescent salt, of a blue green colour; it may be formed by digesting either oxide in muriatic acid; if the peroxide be used, chlorine is evolved, and it passes to the state of protoxide. When a little diluted, this solution becomes pink; the pale pink solution, when written with, is scarcely visible; but if gently heated, the writing appears brilliant and green, which soon vanishes as the paper cools, in consequence of the salt absorbing the aerial moisture. This solution has been termed *Hellot's sympathetic ink*. It may be prepared as follows.

Muriate.

Sympathetic Ink.

One part of cobalt, or, still better, of zaffre, may be digested in a sand heat, for some hours, with four parts of nitric acid. To the solution, add one part of muriate of soda; and dilute with four parts of water. Characters written with this solution are illegible when cold; but when a gentle heat is applied, they assume a beautiful blue or green colour. This experiment is rendered more amusing by drawing the trunk and branches of a tree in the ordinary manner; and tracing the leaves with a solution of cobalt. The tree appears leafless, till the paper is heated, when it suddenly becomes covered with beautiful foliage. The addition of a little nitrate of copper to the solution forms a sympathetic ink, which by heat gives a rich greenish yellow colour. When a small quantity of muriate of soda, of magnesia, or of lime, is added to the ink, its traces disappear very speedily on removal from the fire, showing that the vivid green, blue or yellow colour is owing to the concentration of the saline traces by heat, and their disappearance, to the re-absorption of moisture. U. 346.

1434. With nitric acid the oxide of cobalt furnishes a red *nitrate of cobalt*; the crystals are small prisms of a red colour, composed, according to Dr Thomson, of 1 atom of acid, 1 of protoxide, and 6 atoms water. They are deliquescent in the air and decomposable by heat, leaving a deep red powder. When thrown into a flask full of liquid potassa, a blue precipitate is formed, which, if the flask be immediately closed, passes to violet, and afterwards to red, by becoming the *hydrate* or *hydrated oxide* of cobalt. This compound is soluble in cold carbonate of potassa and tinges it red. The oxide is not soluble in this liquid. The hydrate loses from 20 to 21 per cent. of water by heat, and is reduced to protoxide. Solutions of cobalt are precipitated by carbonated alkalies, at first of a peach-flower colour, and afterwards of a lilac hue. H. 2. 89.

Nitrate.

1435. Ammonia digested upon recently precipitated protoxide of cobalt slowly dissolves it, and forms a pale pink solution, which becomes deeper coloured by exposure to air, in consequence of the metal passing to the state of peroxide. The ammoniacal solution of the peroxide forms acicular crystals of a beautiful pink colour.

Action of ammonia.

1436. *Cobalt and Sulphur*.—Cobalt may be brought to combine directly with sulphur and with phosphorus. According to Proust the sulphuret is composed of cobalt 71,5 sulphur 28,5.

Sulphurets.

M. Sitterberg has found that the deutoxide of cobalt decomposes sulphuretted hydrogen gas when cold. The sulphuret thus produced contains three atoms of sulphur. Muriatic acid dissolves some of the cobalt in it, and leaves another sulphuret

of cobalt in the form of a black powder, which contains 4 atoms of sulphur for 1 of metal.* The deuto-sulphuret may be formed by mixing finely divided oxide of cobalt with three times its weight of sulphur, and heating to very dull redness, until no more sulphur sublimes. It consists of 100 cobalt + 109 sulphur. It is reduced to grey proto-sulphuret by strong heat.†

Sulphate.

1437. *Sulphate of Cobalt*.—Sulphuric acid does not attack cobalt unless when concentrated and heated; nor does it readily dissolve the oxide. They may, however, be brought to combine, and the result is a salt in oblique rhombic prisms.‡

Anhydrous sulphate.

When dried at a temperature of 500°, the crystals fall into a blue powder, which in a bright heat fuses and gives out sulphuric acid, leaving a black oxide. The blue powder is the *anhydrous sulphate of cobalt*, perfectly soluble in water, and forming a pink solution; it is slightly deliquescent, and becomes lilac coloured by exposure to air.

Phosphate.

1438. Sulphate of cobalt forms triple compounds with potassa and with ammonia, if it contain nickel, the crystals are of a greenish tinge, but pink when the cobalt is pure.§

1439. *Phosphate of Cobalt* may be formed by decomposing the muriate of cobalt with phosphate of soda; it is insoluble, of a lilac colour, and if mixed with eight parts of gelatinous alumina and heated, it produces a beautiful blue, which may sometimes be employed by painters as a substitute for ultramarine.|| This salt was obtained by Dr Thomson by dissolving carbonate of cobalt in phosphoric acid, and mixing the solution with alcohol: a copious precipitate falls, which was collected on a filter,edulcorated, first with alcohol and then with water. It was gelatinous and had a fine crimson colour. When dried, it conercted into a hard dark red matter which reddened vegetable blues.¶ Dr Thomson considers it as composed of 1 atom phosphoric acid, 1 protoxide of cobalt, and 2 of water.

Carbonate.

1440. *Carbonate of Cobalt* is formed by decomposing the nitrate, muriate, or sulphate of cobalt by carbonate of potassa or soda; a reddish blue powder is precipitated which should be washed thoroughly with water. When dry, it is a light powder, having a light pink colour. It is tasteless, insoluble in water, and not altered by exposure to the air. It does not alter vegetable blues, but dissolves in acids with effervescence. It consists of 1 atom carbonic acid, 1 protoxide of cobalt and 1 water. T.

1441. Ferro-cyanate of potassa forms a grass green precipitate in solutions of cobalt.

Borate.

1442. Solution of borax produces a pink precipitate in solution of muriate of cobalt, which is probably a *borate of cobalt*.

* *Edin. Jour.* iv. 136.

† *Quart. Jour.* N. S. iv. 476.

‡ Dr Thomson has also described a *bi-sulphate*, consisting of 2 atoms acid, 1 of base and 3 atoms of water.

§ *Hydrosulphuretted Oxide of Cobalt* is precipitated from the muriate by hydrosulphuret of ammonia, of a black colour. *Phosphuret of Cobalt* is a white brittle compound.

|| For a full description of the process see Thenard, *Traité de Chim.* Ed. 4, vol. 3d, p. 146.

¶ T. *First Principles*, ii. 344.

1443. The salts of cobalt all contain the protoxide; they are decomposed by ammonia, which, if added in excess, re-dissolves the oxide: phosphoric, carbonic, arsenic, and oxalic acids, produce, by double decomposition, insoluble red or lilac precipitates in these solutions. Decomposition of salts of cobalt.

1444. The alloys of cobalt are unimportant.

1445. The chief use of cobalt is as a colouring material for porcelain, earthenware, and glass; it is principally imported from Germany in the state of *zaffre*, and *smalt*, or *azure*. Uses.

The colouring power of oxide of cobalt on vitrifiable mixtures, is greater perhaps, than that of any other metal. One grain gives a full blue to 240 grains of glass. U.

Zaffre is prepared by calcining the ores of cobalt, by which sulphur and arsenic are volatilized, and an impure oxide of cobalt remains, which is mixed with about twice its weight of finely powdered flints. Zaffre.

Smalt and *azure blue* are made by fusing *zaffre* with glass; or by calcining a mixture of equal parts of roasted cobalt ore, common potash, and ground flints. In this way a blue glass is formed, which, while hot, is dropped into water, and afterwards reduced to a very fine powder. Smalt.

SECTION XX. Uranium.

1446. This metal was discovered by Klaproth, in 1789, in a mineral called *pitchblende*, which contains uranium combined with sulphur, and according to Arfwedson, arsenic, cobalt, and zinc.* Discovery.

From this ore uranium may be obtained by the following process: reduce it to powder, and expose it to heat in a muffle; then digest in dilute nitro-muriatic acid, and precipitate by excess of ammonia, to retain oxide of copper; collect and wash the precipitate, and dry it at a heat approaching redness. Process for obtaining the metal.

When exposed to a violent heat with a small quantity of charcoal powder, metallic uranium is obtained.

M. Arfwedson has succeeded in reducing the protoxide of uranium to a metallic state, by passing a current of dry hydrogen gas over it while hot. The metal thus obtained was in crystals, having nearly the form of regular octoëdrons, with a strong metallic lustre, and a reddish brown colour. Arfwedson's.

Its specific gravity has not been ascertained with precision. Bucholz states it as = 9.0.†

1447. Uranium may be exposed to the air in ordinary temperatures without alteration, but when heated it undergoes a kind of combustion, and is converted into a black oxide.

1448. *Uranium and Oxygen*.—Uranium unites with oxygen in two proportions. The composition of these oxides has been Oxides.

* *Mem. Acad. Sci. of Stockholm*, 1822.

† *Gehlen's Journal*, iv.

minutely studied by Arfwedson* and Thomson.† According to the last mentioned chemist the weight of an atom of uranium is 208, and its oxides are thus composed,

| | Uranium | Oxygen. |
|-------------------|---------|------------|
| Protoxide | 208 | — 8 = 216 |
| Peroxide | 208 | — 16 = 224 |

According to the analysis of Arfwedson 216 is the atomic weight of uranium, and the oxygen in its two oxides is in the ratio of 1 to 1,5 : and Berzelius has arrived at a similar conclusion.

Protoxide.

1449. *Protoxide of Uranium* is of a dark green colour, and is obtained by decomposing the nitrate of the peroxide by heat. It is exceedingly infusible, and bears any temperature hitherto tried without change. It unites with acids, forming salts of a green colour. It is readily oxidized by nitric acid, and yields a yellow solution, which is a nitrate of the protoxide.

The protoxide is employed in the arts for giving a black colour to porcelain. T.

Action of reagents.

1450. Caustic ammonia precipitates the protoxide of uranium from its solutions in brown flocks inclining to purple, forming a hydrate; and when this is dried, the protoxide generally passes in great part to the state of peroxide. Carbonate of ammonia throws down from the proto-salts a light green precipitate of proto-carbonate of uranium, which is again dissolved by an excess of the precipitant. The hydrated protoxide dissolves very easily in acids, but if digested for an hour in water, the chemically combined water separates; the matter concretes into a heavy powder of small bulk, and is afterwards acted upon with great difficulty by acids.

Peroxide.

1451. *Peroxide of Uranium* performs the double function of an acid and a base, and has so strong a tendency to enter into combination with other oxidized bodies, that it has not yet been obtained in an insulated state. If, for instance, we precipitate a solution of this oxide in nitric or muriatic acid by caustic ammonia, the precipitate is a combination of peroxide of uranium with ammonia and water, not decomposable by washing. It has probably a lemon colour, for this is the colour by which most of its salts are distinguished. H. 2. 81.

Nitrate.

1452. This metal is most soluble in nitric acid. The *Nitrate* forms prismatic brownish yellow crystals, which have a peculiar iridescent appearance, are deliquescent, and are constituted according to Bucholz.‡ of 61 base, + 25 acid + 14 water.§

Characteristics of salts of uranium.

1453. The salts of uranium have a yellow colour and an astringent metallic taste. Potassa forms in their solutions a

* *Ann. of Philos.* N. S. vii.

† *First Prin.* ii.

‡ *Gehlen's Jour.* iv.

§ *Subnitrate of Uranium*, upon the authority of Bucholz, is formed by heating the nitrate, which renders a part insoluble in water, and separates in the form of a yellow powder.

Uranium according to Berzelius has a very weak affinity for sulphur. *Sulphuret of Uranium* exists native. Neither the *Hyposulphite* nor *Sulphite of Uranium* have been examined.

Sulphate of Uranium forms yellow prismatic crystals, decomposable by heat, and according to the analysis of Bucholz, consisting of 70 oxide, 18 acid and 12 water.

yellow precipitate, and carbonate of potassa a white precipitate; both these precipitates are insoluble in excess of pure alkali, but dissolve in the carbonate.* Ferro-cyanate of potassa produces a rich brown precipitate in solutions of uranium, which is very characteristic.

1454. Among the *native compounds of uranium*, the green uran mica appears, from the experiments of Mr R. Phillips, to consist of phosphoric acid, peroxide of uranium, oxide of copper, and water; and the yellow, from the analysis of Berzelius, of similar ingredients, with the substitution of phosphate of lime for phosphate of copper. The first may be considered as a double sesqui-phosphate of uranium and copper, and the second of uranium and lime. A native proto-sulphate of uranium in beautiful emerald green crystals has been also discovered, and a sub-persulphate, forming an intense sulphur yellow coating over the surface of the minerals on which it is found. H.

SECTION XXI. Titanium.

1455. Titanium, in the metallic state, was discovered by Dr Wollaston, in 1822, in the slag at the bottom of the iron smelting-furnace at Merthyr Tydvil in South Wales.† It is found also in octoëdral iron from Corsica, and in the specular iron ore of Elba. It has been since found in several other places in Europe. It has the form of small smooth cubes, having a red colour, exceedingly similar to that of copper. The cubes are hard enough to scratch rock crystal, and cannot be fused by the highest temperature which can be raised by the blow-pipe. The specific gravity, as determined by Dr Wollaston, is 5.3.‡ From the situation in which this metallic titanium has been found, we may infer that it does not combine with iron, and Dr Wollaston tried in vain to unite it with lead, tin, silver and copper. It does not appear, however, to be absolutely free from iron; Dr Wollaston found that when suspended by a fine thread a magnet drew it about 20 degrees from the perpendicular. He succeeded in detecting the presence of iron in it, and calculated the amount of that metal at $\frac{1}{250}$ th part of the weight of the titanium.§

Discovery of metallic titanium.

1456. Titanium is susceptible of two degrees of oxidizement. The *Protoxide* is blue, and occurs native in crystals, called *anatase*. Little is known of the properties of this oxide.

Ox. des.

* Dr Thomson found that the precipitate obtained by caustic soda, from the solution of the pernitrate, was re-dissolved by an excess of the alkali. *First Prin.* ii. 8.

† *Philos. Trans.* 1823.

‡ From the extreme infusibility of the cubes of metallic titanium, Dr Wollaston infers that they have not been formed by crystallization in cooling from a state of fusion; but from the reduction of the oxide dissolved in the slag around them.

§ *Phil. Trans.* p. 200. Thomson's *First Princip.* 2. 80.

1457. The *peroxide* is white, and possessing some of the properties of a weak acid, it is called by Rose* *titanic acid*.† It exists nearly pure in *titanite* or *rutile*. The *menachanite* in which titanium was originally discovered by Mr Gregor is a compound of the oxides of titanium, iron and manganese. The oxide is best prepared from rutile.

Process for
obtaining
the metal.

1458. The metal may be obtained from titanite by fusion with potassa; the fused mass, washed with water, leaves oxide of titanium, containing a little iron; it is to be dissolved in muriatic acid, and precipitated by oxalic acid. B.

1459. From menachanite, white oxide of titanium may be obtained by fusing with potassa, and adding muriatic acid to the alkaline solution.

Reduction of
the oxide.

1460. The oxide of titanium fuses, but is not reduced by a powerful galvanic battery. It is reduced, however, by exposure to an intense heat, moistened with oil, and surrounded by powdered charcoal, a blackish blistered substance is obtained, some points of which have a reddish colour. Like columbic acid and silica (which Rose considers as an acid) its affinities are exceedingly weak. When heated to redness it becomes yellow, but regains its whiteness on cooling; it is found, however, to have become insoluble in acids. When precipitated titanic acid is digested in water, the liquid passes milky through several folds of paper. Hence it cannot be collected on a filter, but this property is destroyed by an acid, an alkali, or a neutral salt. When fused with potassa and dissolved in muriatic acid it gelatinates. H. 2. 92.‡

Separation of
titanic acid
from iron.

1461. There is great difficulty in separating titanic acid, or peroxide, from oxide of iron; the best process appears to be that lately discovered by M. Rose, which also facilitates the separation of the acid from its more abundant compounds.§ A solution of titanic acid, and oxide of iron being obtained in muriatic acid, if tartaric acid be added to it, and the whole be diluted with water, a great excess of caustic ammonia may be added without any precipitation of titanic acid, or oxide of iron. If to this solution hydrosulphuret of ammonia be added, it exerts no action on the titanic acid, but changes all the oxide of iron into sulphuret, which separates, perfectly. This precipitate is to be carefully washed with water, containing a few drops of hydrosulphuret of ammonia, until all the tartrate is removed: it is then to be dissolved in muriatic acid, heated to drive off the sulphuretted hydrogen, treated with nitric acid to peroxidize the iron, and then precipitated by ammonia: in this way the

* *Ann. of Philos.* N. S. vi. 369.

† According to M. Peschier, *Ann. de Chim.* xxvii. 281, titanium forms double salts with all the acids.

‡ The oxalate of titanium affords the metal by intense ignition with charcoal, it is, however, scarcely possible to obtain it in any state of agglutination: in some trials made in the Royal Institution, nothing like globules of the metal could be procured, and the crucibles were always fused. B.

§ *Quarterly Journal*, No. xxxix.

iron is procured. The titanitic acid may be separated from the solution (if it contain no fixed parts,) by evaporating to dryness, and heating red-hot in contact with air, until all that is volatile is dissipated, and the charcoal is burnt off. This is best done in a small platinum crucible in a muffle; titanitic acid remains.*

1462. *Chloride of titanium* was formed by Mr George, by Chloride. passing dry chlorine over the pulverized ashes from the iron slag. A fluid condensed in the cool part of the tube which was transparent, colourless, emitted dense white fumes, and boiled violently at a temperature little exceeding 212° F. on adding a drop of water to a few drops of this liquid, an almost explosive disengagement of chlorine ensued; and when the water was not in excess, a white salt was formed, the solution of which had all the properties of muriatic acid of titanium. There appears from these experiments to be two chlorides, the one constituted of about 64 titanium with 36 chlorine, the other with 72. H.†

1463. *Sulphuret of Titanium* was formed by Rose, by pass- Sulphuret. ing sulphuret of carbon over titanitic acid strongly heated in a porcelain tube. It is of a deep green colour, and, when rubbed with a hard substance, assumes a very strong metallic lustre like that of brass. It becomes very hot when nitric acid is poured upon it, nitrous gas is disengaged, and titanitic acid is deposited in the state of a fine powder. The analysis of the bi-sulphuret by combustion gave,

| | |
|------------------|-------|
| Titanium | 49,17 |
| Sulphur | 50,83 |
| | <hr/> |
| | 100 |

And that of the titanitic acid

| | |
|------------------|-------|
| Titanium | 66,05 |
| Oxygen | 33,95 |
| | <hr/> |
| | 100 |

1464. From a review of the experiments of Rose and his own Atomic weight. investigations, Dr Thomson is induced to consider 48 as the true atomic weight of titanitic acid, 40 as that of the protoxide, and 32 that of titanium.‡

1465. The solutions of titanium are colourless, and afford Tests. white precipitates with the alkalies; ferro-cyanate of potassa gives a precipitate of a red colour inclining to orange, and infu-

* This method may be followed with minerals containing titanitic acid combined with protoxide of iron, which may be pulverized and dissolved in strong muriatic acid. *Ann. de Chim.* xxxix. 130

† *Ann. of Philos.* N. S. ix. 18.

The carbonate of titanium dissolves in muriatic, nitric, and sulphuric acids, and phosphoric acid occasions a white precipitate in these solutions. Neither the *muriatic*, *nitric*, nor *sulphuric* are crystallizable. The solution of the muriatic is speedily decomposed by exposure to light, and a white precipitate of oxide is formed in it.

When the native oxides of titanium are fused with carbonate of potassa, at a temperature not too high, a white carbonate of titanium is formed.

‡ *First Prin.* ii. 80.

sion of galls a similar one, which, if the solution be concentrated, has the appearance of coagulated blood. A rod of tin, immersed in the solution, imparts to the liquid around it a fine red colour; and a rod of zinc, a deep blue one.

SECTION XXII. *Cerium.*

1466. THIS metal was obtained by Hisinger and Berzelius, from a mineral found at Bastnas in Sweden, to which they have given the name of *Cerite*.* It is also contained in *Allanite*, a mineral from Greenland, first distinguished as a peculiar species by Mr Allan, of Edinburgh. It contains, according to Dr Thomson's analysis, about 40 per cent. of oxide of cerium.

How obtained.

The ore is calcined, pulverized, and digested in nitro-muriatic acid. To the filtered solution saturated with potassa, oxalic acid is added, which occasions a precipitate; this, when dried and ignited, is oxide of cerium.

This oxide is extremely difficult of reduction. Mr Children succeeded in fusing it by the aid of his powerful Voltaic apparatus, and when intensely heated it burned with a vivid flame, and was partly volatilized.

Vauquelin's experiments.

1467. The attempts of Vauquelin to reduce the oxide of cerium produced only a small metallic globule, not larger than a pin's head. This globule was not acted upon by any of the simple acids; but it was dissolved, though slowly, by nitro-muriatic acid. The solution was reddish, and gave traces of iron; but it also gave evident marks of cerium, by the white precipitate which tartrite of potassa and oxalate of ammonia threw down. The metallic globule, also, was harder, whiter, much more brittle, and more scaly in its fracture, than pure cast-iron. The oxide fused by Mr Children's battery, on exposure for a few hours to the air, fell into a light brown powder, containing numerous particles of a silvery lustre. Hence cerium appears to be a volatile metal, unless it be volatilized in the state of an oxide, which remains to be decided by future experiments. H. ii. 78.

Oxides.

1468. *Cerium and Oxygen.* Cerium unites with oxygen in two proportions, and the composition of the resulting oxides has been particularly studied by M. Hisinger.† Dr Thomson has likewise made experiments on this subject, and infers that 50 is the atomic weight of cerium, and that its oxides are thus constituted—

| | Cerium. | Oxygen. | |
|-------------------|------------|------------|------|
| Protoxide | 50 | 8 | = 58 |
| Deutoxide | 50 | 12 | = 62 |

* The name *Cerium* was given to this metal from the planet *Ceres*, discovered about the same period. See Nicholson's Jour. xii. 105.

† *Ann. of Philos.* iv.

1469. The *Protoxide* of cerium is a white powder, which is insoluble in water, and forms salts with acids, all of which, if soluble, have an acid reaction. It is obtained from *cerite*, which, after being calcined and pulverized, is dissolved in nitro-muriatic acid; the solution is filtered, neutralized with pure potassa, and then precipitated by tartrate of potassa, or as Laugier recommends, by oxalic acid. This precipitate, well washed and calcined, is the oxide of cerium. Protoxide.

1470. The *Peroxide* of cerium is of a fawn red colour. Muriatic and sulphuric acids dissolve it, and the solutions afford yellow crystals. The muriate is deliquescent; the sulphate difficultly soluble. The sulphate of the protoxide forms white crystals of a sweet taste. Nitric acid forms with the protoxide a deliquescent compound, of a sweet taste. The carbonate is precipitated from these solutions in the form of a white powder. Peroxide.

1471. *Sulphuret of Cerium* may be prepared according to Dr Mosander, in the following manner. Sulphuret.

Carburet of sulphur is to be passed in vapour over the carbonate of cerium heated to redness; the sulphuret of cerium produced is red, resembling minium in appearance, porous, light, not alterable either in air or water. When oxide of cerium is fused with sulphuret of potassa in great excess, at a white heat, a sulphuret is also formed, which may be obtained separate by washing. It appears as small brilliant scales resembling mosaic gold in powder, but, under the microscope, appearing to be transparent and of a yellow colour. These apparently different varieties of the substance dissolve readily in acids, evolving sulphuretted hydrogen gas, and yielding no residue of sulphur. The compound consists of 74 parts of cerium and 26 sulphur.*

1472. The salts of cerium are either white or yellow, as they contain either the protoxide or peroxide. Their neutral solutions taste sweet. Ferro-cyanate of potassa, and oxalate of ammonia, produce white precipitates soluble in nitric and muriatic acids. Neither sulphuretted hydrogen, nor gallic acid, occasion any precipitate. B. Salts of cerium.

An infusion of galls produces, in muriate of cerium, a yellowish precipitate not very abundant. A few drops of ammonia throw down a very voluminous one of a brown colour, which becomes black and brilliant, by desiccation. By the action of heat, it assumes a brick-red colour. H. ii. Testa,

SECTION XXIII. Tellurium.

1473. THE ores of tellurium are, 1. *Native*, in which the metal is combined with iron and a little gold. 2. *Graphic ore*, Ores.

* *Ann. de Chim.* xxxiii. 100.

a compound of tellurium, gold, and silver. 3. *Yellow ore*, a compound of tellurium, gold, lead, and silver; and 4. *Black ore*, consisting of the same metals, with copper and sulphur.

These ores have been found in the Transylvania mines, in Siberia, and at Huntington in the state of Connecticut.*

Tellurium was discovered by Klaproth,† in an ore of gold.

Process for
obtaining
tellurium.

His process for extracting it consists in the solution of the ore by nitro-muriatic acid, dilution with water, and the addition of pure potassa, which throws down all the metals that are present; and, when added in excess, re-dissolves a white precipitate which it at first occasions. To the alkaline solution, muriatic acid is then added; a precipitate again appears; and this, when dried and heated with one-twelfth its weight of charcoal, or with a small quantity of oil, in a glass retort, yields tellurium, in the form of small brilliant metallic drops, lining the upper part of the body of the retort.—One hundred parts of the ore yield above 90 of tellurium. H. 2. 112.

Properties.

1474. Tellurium is of a bright grey colour, brittle, easily fusible, and very volatile. Its specific gravity is 6,1.

Oxide.

1475. It is oxidized when heated in contact with air; and burns with a sky-blue flame, edged with green. Upon charcoal, before the blow-pipe, it inflames with a violence resembling detonation; exhibits a vivid flame; and entirely flies off in a grey smoke, having a peculiarly nauseous smell.‡ This smoke, when condensed, and examined in quantity, is found to be white with a tint of yellow. It is fusible by a strong heat, and volatile at a still higher temperature. It not only unites as a base with acids, but also itself possesses the character of an acid, and forms a class of salts, which may be called *tellurates*. It is composed, according to Klaproth, of

| | | | | |
|-----------|-----------|----|-------|------|
| Tellurium | | 83 | . . . | 100, |
| Oxygen | | 17 | . . . | 20,5 |
| <hr/> | | | | |
| 100 | | | | |

Weight of
its atom.

Berzelius, however, determines the quantity of oxygen, absorbed by 100 of tellurium, when changed into oxide, to be 24,1. If this result be correct, and the compound be the protoxide, the atom of tellurium should weigh 32, and the oxide 40.

Action of
nitric acid.

1476. Tellurium is soluble in nitric and nitro-muriatic acids. The saturated solution is decomposed by the mere addition of water, which throws down a white powder; but this is again dissolved on adding more water. Chlorine unites with tellurium, and forms a white semi-transparent compound, which is decomposed when added to water. It consists, according to Sir H. Davy, of 100 tellurium united with 90,5 chlorine. From its solutions it is precipitated in a metallic form, by iron, zinc, tin, and even by muriate of tin. Carbonated and pure alkalies precipitate the telluric oxide united with water, in the form of a white hydrate; and the oxide is re-dissolved by an excess of alkali or carbonate. Alkaline sulphurets throw down a dark

— of chlorine

* Amer. Jour. of Science, i. 405.

† Contributions, ii. 1.

‡ Ascribed by Berzelius to the presence of selenium.

brown or blackish precipitate. Tincture of galls produces a flocculent yellow precipitate. The solutions of this metal in acids are not decomposed by prussiate of potassa; a property which tellurium possesses in common with gold, platinum, iridium, rhodium, osmium, and antimony. H. 2. 113.

1477. It gives a deep purple colour to sulphuric acid, from which it is thrown down in black flocculi by water; but if the acid be diluted with two or three parts of water to which a little nitric acid has been added, a large portion of the metal is dissolved, and the solution is not decomposed by water. U. 742.

— of sulphuric acid.

1478. Tellurium forms two distinct compounds with hydrogen, the one of which is solid, and the other gaseous. 1st. By making tellurium the negative surface in water, in the galvanic circuit, a brown powder is formed, which is a solid *hydruret of tellurium*. 2dly. By acting with dilute sulphuric acid, upon the alloy of tellurium and potassium (which may be obtained by heating a mixture of solid hydrate of potassa, tellurium, and charcoal), we obtain a peculiar gas. This gas has a smell resembling that of sulphuretted hydrogen. It is absorbed by water, and a claret-coloured solution results, which, by exposure to the air, becomes brown, and deposits tellurium. After being washed with a small quantity of water, it does not affect vegetable blue colours. It burns with a bluish flame, depositing oxide of tellurium. It unites with alkalies; precipitates most metallic solutions; and is instantly decomposed by chlorine gas. It may be called *telluretted hydrogen gas*. According to Berzelius, it is constituted of 100 parts of tellurium with a little less than two parts of hydrogen. It probably consists, Dr Thomson thinks, of 1 volume of tellurium vapour and 1 vol. of hydrogen gas condensed into 1 vol. H. 11. 114.

Union with hydrogen.

1479. According to Dr Thomson, the specific gravity of telluretted hydrogen is 2,916, and 100 cubical inches weigh 69,895 grains.

1480. *Tellurate of Potassa* may be formed by heating oxide of tellurium with nitre, and dissolving the residuum in boiling water, which, on cooling, deposits an imperfectly crystallized white powder, difficultly soluble in water.

Tellurate of potassa.

1481. Solution of tellurate of potassa, added to solutions of lime, baryta, strontia, copper, and lead, forms insoluble tellurates of the oxides of those metals.

SECTION XXIV. Arsenic.

1482. ARSENIC, as it is found under that name in the shops, is not a metal, but a white oxide, from which the metal may be

To obtain metallic arsenic.

obtained by mixing it with half its weight of black flux,* and introducing the mixture into a Florence flask, placed in a sand bath, gradually raised to a red heat; a brilliant metallic sublimate of pure arsenic collects in the upper part of the flask. The volatility of white arsenic prevents its easy reduction by charcoal alone; but the potassa in the flux enables it to acquire a temperature sufficient for its perfect reduction.

Characters.

1483. Arsenic is of a steel blue colour, quite brittle, and of a specific gravity = 8,3. It readily fuses, and in close vessels may be distilled at a temperature of 360° , which is lower than its fusing point. Its vapour has a very strong smell, resembling that of garlic. Heated in the air it easily takes fire, burns with a blue flame, and produces copious white fumes of oxide. Exposed to a moist air it gradually becomes incrustated with a grey powder, which is an imperfect oxide. This metal and all its compounds are virulent poisons.

1484. *Native arsenic* usually occurs in rounded masses, or nodules, of a foliated lamellar texture, in the veins of primitive rocks, and is often associated with silver, cobalt, lead, and nickel ores.

Oxides.

1485. *Arsenic a. d Oxygen*.—There are two definite compounds of arsenic and oxygen, which are both capable of forming combinations with other metallic oxides. They are sour and soluble in water, and have thence been properly termed *arsenious* and *arsenic acids*.

Arsenious acid.

The arsenious acid, or, as it is commonly called, *white arsenic*, or *white oxide of arsenic*, is the best known, and most commonly occurring compound of this metal; and as cases of poisoning by it are frequent, every person should be well acquainted with its characteristic properties.

How obtained.

1486. Arsenious acid may easily be procured by the combustion of the metal; but as it is formed during certain metallurgical processes, that mode is rarely resorted to. It is abundantly prepared at Joachimsthal in Bohemia, from arsenical cobalt ores, which are roasted in reverberatory furnaces, and the vapours condensed in a long chimney, the contents of which, submitted to a second sublimation, afford the *white arsenic* of commerce.

Properties.

1487. Arsenious acid is white, semi-transparent, brittle, and of a vitreous fracture. Its specific gravity is 3,7. Its taste has been usually described as acrid, but from recent experiments† it appears that this is incorrect. It is virulently poisonous, producing inflammation and gangrene of the stomach and intestines; it also proves fatal when applied to a wound; and as the local injury is in neither case sufficient to cause death, it is

Black flux

* This is an extremely useful compound for effecting the reduction of many of the metallic oxides. It consists of charcoal and subcarbonate of potassa, and is best prepared by deflagrating in a crucible a mixture of one part of nitre and two of powdered tartar. The mixture remains in fusion at a red heat, and thus suffers the small globules of reduced metal to coalesce into a button.

† See Dr Christison's experiments. *Edin. Philos. Jour.* xiv. 380.

probable that an induced affection of the nervous system and of the heart is the cause of the mischief.* To get rid of the poison by producing copious vomiting and purging, and to pursue the usual means of subduing and preventing inflammation, are the principal points of treatment to be adopted in cases where this poison has been taken.†

1488. By a slow sublimation arsenious acid forms tetraëdral crystals; it is volatile at 380°, and has no smell when perfectly free from metallic arsenic.‡ According to Klaproth, 1000 parts of water at 60° dissolve 2,5 of white arsenic,§ and 1000 parts of water at 212°, dissolve rather more than 77 parts, and about 30 parts are retained in permanent solution.—But the most elaborate experiments are those of Fischer of Breslau. According to these, white oxide of arsenic is insoluble as such in water, and when acted upon by water, one portion of the oxide acquires oxygen from another, and, becoming acidified, is rendered soluble. This is the reason why the undissolved portion loses its colour, and becomes of a dirty yellow. Of boiling water, 12,3 parts dissolve one of arsenic; but at the common temperature of the atmosphere, 66½ parts of water take up only one part.|| H.

Action of water.

The solutions redden vegetable blues. The oxide is soluble in 70 or 80 times its weight of alcohol, and in oils. Its aqueous solution furnishes tetraëdral crystals by slow evaporation.

1489. Considerable difference of opinion exists as to the composition of these acids. Berzelius maintains that the oxygen of arsenious acid is to that of arsenic acid as 3 to 5, while Dr Thomson contends that the ratio is as 2 to 3.

Ratio of the oxygen in arsenic and arsenious acids.

1490. From late experiments Dr Thomson has deduced the weight of the atom of arsenic to be 4,75 oxygen being 1; this corresponds with 38 when hydrogen is taken as unity; and he considers arsenious acid as composed of 1 atom arsenic and 2 atoms oxygen; and arsenic acid of 1 arsenic + 3 oxygen, giving 6,75 for the representative number of arsenious acid on the oxygen scale, or 54 on the hydrogen; and arsenic will be acid represented on the former by 7,75, on the latter by 62.¶

Equivalent number.

1491. Native White Arsenic occurs in prismatic crystals, and in a pulverulent form; it is found in Saxony and Hungary.

Arsenites.

1492. The arsenious acid forms a distinct class of salts, called *arsenites*, which have been but little examined.

The *arsenites of ammonia, potassa, and soda*, are easily soluble and uncrystallizable; they are formed by boiling the

* Brodie's *Observations and Experiments on the Action of Poison*. Phil. Trans. 1812.
† Orfila, *Traite des Poisons*, Tom. i. p. 123.
‡ Dr Paris, *Quarterly Journal of Science and Arts*, vol. vi.
§ It would take a long time to prepare a saturated aqueous solution of white arsenic, by contact of the powder with water, or even by agitation; but by boiling the water with the powder for half an hour, leaving it to cool, and afterwards filtering it, a saturated solution will be at once obtained.—Faraday, *Chem. Manip.* 174.
|| Thomson's *Annals*, vii. 33.
¶ See *First Princip.* 2.

acid in the alkaline solutions. Those of *lime, baryta, strontia*, and *magnesia*, are difficultly soluble, and formed in the same way. Arsenite of potassa is the active ingredient in the *liquor potassæ arsenitis* of the *U. S. Pharmacopœia*, and in *Fowler's mineral solution* or *tasteless ague drop*.

Arsenite of ammonia produces a yellow precipitate in nitrate of silver, easily soluble in excess of ammonia.

— of potassa. 1493. Arsenite of potassa produces a white precipitate in the white salts of manganese; a dingy green precipitate in the solutions of iron; a white precipitate in solutions of zinc and tin. Mixed with a solution of sulphate of copper, a precipitate of a fine apple green colour falls, called from its discoverer, *Scheele's green*, and is useful as a pigment. In the solutions of lead, antimony, and bismuth, it forms white precipitates: added to nitrate of cobalt it forms a pink precipitate; and bright yellow, with nitrate of uranium. With nitrate of silver it forms a white precipitate, soon becoming yellow, and very soluble in ammonia. All these precipitates are probably *arsenites* of the respective metals, and, heated by a blow-pipe on charcoal, they exhale the smell of arsenic.

Arsenic acid. 1494. By repeated distillation with nitric acid only, arsenious acid is changed into *arsenic acid*. Or a mixture of 4 parts of muriatic and 24 of nitric acid may be distilled off 8 parts of arsenious acid, gradually raising the bottom of the retort to a red heat at the end of the operation. It may also be procured by distilling nitric acid off powdered metallic arsenic.

Properties. 1495. Arsenic acid is a white substance, of a sour taste; it is deliquescent and uncrystallizable. Its specific gravity is 3.4. It requires for solution 6 parts of cold and 2 of boiling water; its solution reddens vegetable blues.

Arseniates. 1496. Arsenic acid unites with bases, and constitutes a class of salts called *arsenates* or *arseniates*. These salts resemble the phosphates in this as in other respects, that though carefully neutralized when in solution, yet, when concentrated by evaporation, they crystallize with an excess of base. H. 2. 53.

— of ammonia. 1497. *Arseniate of Ammonia* is formed by saturating arsenic acid with ammonia; rhomboidal prisms are obtained on evaporation, which, when gently heated effloresce and evolve ammonia; at a higher temperature pure water is formed, oxide of arsenic sublimes, and nitrogen is evolved, a circumstance first observed by Scheele.

— of potassa. 1498. *Binarseniate of Potassa* may either be formed by adding excess of arsenic acid to potassa and evaporation; or by heating to redness, in a Florence flask, a mixture of equal parts of nitre and white arsenic; during the latter operation much nitrous gas is evolved, and on dissolving the residue in water, filtering, and evaporating, quadrangular crystals of binarseniate of potassa are obtained. Macquer was the first who procured this compound, hence it was termed *Macquer's neutral arsenical salt*. It is not easily decomposed by heat alone, and may

be fused and kept red-hot without undergoing other change than losing a little acid, but when mixed with about an eighth of charcoal powder and distilled, metallic arsenic rises, and carbonate of potassa, mixed with a part of the charcoal, remains in the body of the retort. This salt is used in pharmacy for the cure of agues.

Dr Thomson's analysis makes it to consist of

| | | | |
|------------------------|---------|-----|-------------|
| Arsenic acid | 2 atoms | 124 | Composition |
| Potassa | 1 atom | 48 | |
| Water | 1 " | 9 | |
| | | 181 | |

1499. *Arseniate of Soda* is formed by saturating a solution — of soda of carbonate of soda with arsenic acid; on evaporation, crystals are obtained, have the same shape as those of phosphate of soda, and effloresce by exposure to a dry atmosphere.

It has a cooling taste, resembling that of carbonate of soda, but less strong. It requires more than four times its weight of cold water for solution, and the liquid has alkaline properties. It undergoes the watery fusion. Its solution, when dropped into most earthy and metallic salts, occasions precipitates, the peculiar appearances of which are exhibited by Dr Thomson in a table published in the *Annals of Philosophy*, xv. 83. It consists of 1 atom arsenic acid, 1 atom of soda, and 8 atoms of water. There is also a binarseniate of soda, agreeing in the shape of its crystals with bi-phosphate of soda. These crystals consist of 2 atoms of acid, 1 of base, and 5 atoms of water. H. 2. 54.

1500. *Arseniate of Lime* is deposited when arsenic acid is — of lime. dropped into lime-water, or when arseniate of potassa is added to nitrate of lime; it is difficultly soluble in water, and consists, according to Laugier* of arsenic acid 67, lime 33, numbers which do not exactly correspond with 1 proportional of acid + 1 of base.†

* *Ann. de Chim.* 85, 58.
† *Arseniate of Baryta* may be formed by mixing neutral-arseniate of soda with nitrate of baryta; — of Baryta. when the acid is not in excess it is insoluble in water. It consists of

| | | |
|------------------------|-------|--------|
| Arsenic acid | 42.94 | 100, |
| Baryta | 56.06 | 132.88 |
| | | 100. |

Arseniate of Magnesia is soluble, deliquescent, and uncrystallizable. *Arseniate of Manganese* is precipitated in the form of a white powder, by adding arseniate of potassa to muriate of manganese. *Arseniate of Iron*—Arseniate of ammonia, added to the solutions of protosulphate and persulphate of iron, occasions greenish precipitates of *protarseniate* and *perarseniate* of iron, both of which have been examined by Mr Chenevix. *Phil. Trans.* 1801, pp. 220, 225.

Arseniate of Zinc is precipitated in the form of a white insoluble powder when arsenic acid, or an — of zinc. alkaline arseniate, is added to sulphate of zinc.

Arseniate of Tin is a white insoluble powder, precipitated by adding arseniate of potassa to — of tin. muriate of tin.

Arseniate of Copper is formed by adding an alkaline arseniate to nitrate of copper; it is a blue — of copper. insoluble powder. The arseniates of copper have been submitted to an elaborate investigation by Mr Chenevix, he has described five varieties. See *Phil. Trans.* 1801.—Thomson's *System*, ii. 463, Amer. edit. and *First Principles*, ii. 281.

— of lead.

1501. *Arseniate of Lead*.—It may be formed by pouring arsenic acid into any of the soluble salts of lead when it falls in the form of a white powder, insoluble in water, but soluble in dilute nitric acid; a circumstance which enables us in analysis to separate it from sulphate of lead, which is insoluble. This compound is fusible without decomposition; but if it be heated with charcoal, both the lead and arsenic are reduced, and the latter evaporates.

Native.

Arseniate of lead occurs *native*; the finest crystallized varieties are associated with silver at Johanngeorgenstadt in Saxony.* The arseniate from Cornwall, Eng. is inferred by Dr Thomson, from the analysis of Mr Gregor, to consist of 1 atom acid and $1\frac{1}{2}$ protoxide of lead: that from Saxony of 1 atom of each of its constituents. T. 2. 371.†

Chloride.

1502. *Arsenic and Chlorine*.—*Chloride of arsenic* is formed by throwing finely-powdered arsenic into chlorine; the metal burns and forms a whitish, deliquescent, and volatile compound; it may also be obtained by distilling 6 parts of corrosive sublimate with 1 of powdered arsenic; the chloride passes into the receiver in the form of an unctuous fluid, formerly called *butter of arsenic*.‡ Mixed with water, the chloride of arsenic is decomposed, and white oxide, or arsenious acid, is deposited, muriatic acid being at the same time produced. Hence it may be inferred, that the chlorine is to the arsenic in the same proportion as the oxygen, and, consequently, that it consists of 1 proportional of arsenic + 2 proportionals of chlorine, which, from Dr Davy's experiments, appears to be the case.§ B.

Chlorate.

1503. *Chlorate of Arsenic* has not been examined, but chlorate of potassa and metallic arsenic afford a detonating mixture, which takes fire with amazing rapidity.

* Moh's *Mineralogy*, ii, 137.

† *Arseniate of Antimony*.—Nothing is known respecting the combinations of arsenic acid with either of the oxides of antimony. *Arseniate of Bismuth* falls as an insoluble white powder on adding arsenic acid to nitrate of bismuth. *Arseniate of Cobalt* is precipitated of a red colour by the addition of an alkaline arseniate to a soluble salt of cobalt. *Arseniate of Uranium* is thrown down of a straw colour when arseniate of potassa is added to nitrate of uranium.

‡ M. Dumas has given the following process. Put one part of arsenious acid and 10 parts of concentrated sulphuric acid into a tubulated retort, and raise the temperature to nearly 212° F.; then throw fragments of fused common salt into the retort by the tubulure. By continuing the heat and successively adding common salt, proto-chloride of arsenic is obtained: it falls drop by drop from the beak of the retort, and may be collected in cooled vessels; little, if any muriatic acid is disengaged, but towards the end of the operation a portion of hydrated chloride of arsenic is frequently produced which collects in the vessels above the pure chloride. The two bodies do not mix; the hydrate is liquid, transparent and colourless, and more viscid than the dry chloride. The hydrate may be decomposed, and pure chloride obtained, by distilling the mixture from a sufficient quantity of sulphuric acid. *Ann. de Chim et Phys.* xxx iii, 360.

Dr Davy's analysis.

§ Dr Davy determined the composition of this compound|| by synthesis, and states that it consists of

| | | | | |
|----------|-----------|-------|-----------|------|
| Chlorine | - - - - - | 60,48 | - - - - - | 100 |
| Arsenic | - - - - - | 39,52 | - - - - - | 65,3 |

100.

This analysis, however, does not lead to an atomic weight for arsenic at all coinciding with that deduced from the oxides. From the name which Dr Davy gives to this compound, it is evident that he considers it as the proto-chloride; but in that case the atom of arsenic would weigh only 23,5; for 100 : 65 :: 36 : 23,5. There is, probably therefore, some error in the estimate of its composition. H 2. 55.

|| *Philos. Trans.* 1812, 188.

The salt and metal, first separately powdered, may be mixed by the gentlest possible triture, or rather by stirring them together on paper with a knife point. If two long trains be laid on a table, the one of gunpowder, and the other of this mixture, and they be placed in contact with each other at one end, so that they may be fired at once, the arsenical mixture detonates with the rapidity of lightning, while the other burns much less rapidly.*

1504. *Arsenic and Hydrogen*.—When arsenic is presented to nascent hydrogen a portion of the metal combines with the gas. The compound is best obtained by adding a portion of metallic arsenic, or of white arsenic, to the mixture of zinc and dilute sulphuric acid usually employed for the production of hydrogen. It may also be obtained by acting on water with a triple alloy of arsenic, potassium, and antimony. This alloy may be formed by heating strongly, for two hours, in a close crucible, two parts of antimony, two of cream of tartar, and one of white arsenic. When two or three drachms of this alloy are thrown quickly under a jar inverted in water, abundance of *arsenuretted hydrogen* is disengaged†. The greatest caution should be used to avoid its deleterious effects, which were fatal to the late M. Gehlen.‡ The gas may be collected over water, by which it is not sensibly absorbed.

1505. The specific gravity of this gas is liable to vary according to the mode by which it is procured. After standing a day over water, it deposits a small quantity of brown matter, which appears to be a *hydruret of arsenic*, and then it has a specific gravity of from 12 to 14, hydrogen being = 1. This is considerably heavier than the usual estimation. If the gas were composed of 1 proportional of arsenic and two of hydrogen, without condensation, 100 cubical inches should weigh 51,75 grains, and its specific gravity to hydrogen would be 20,7. But Gay-Lussac and Thenard§ have shown by decomposing it by tin, that 100 parts expand to 140, which would still increase its specific gravity, it being probable that 3 volumes of hydrogen are condensed into 2. It is probable, therefore, that the gas, hitherto described under the name of *arsenuretted hydrogen*, is a mixture of the real compound with hydrogen. B.

1506. The gas obtained by the above described process is expanded in volume, and deposits arsenic at high temperatures: exposure to intense cold is said to occasion its liquefaction. It smells strongly alliaceous; it extinguishes a taper, and burns with a pale blue flame, depositing arsenic and its oxide.||

* *Iodide of Arsenic*, obtained by heating the metal with excess of iodine; is of a deep red colour, and volatile. When acted upon by water, it produces hydriodic and arsenic acids. It appears probable that it contains 1 proportional of arsenic and 3 of iodine.

† *Quarterly Journal*, xiii. 225.

‡ *Ann. de chim.* 95, 110; and *Ann. de Chim. et Phys.* iii. 135.

§ *Recherches Physico-Chimiques*, Tom. i. p. 230. From the analogy of the other compounds of hydrogen and a combustible, there seems little doubt that it is a compound of

1 volume arsenic vapour } condensed into 1 volume
1 volume hydrogen gas }

Iodine.

T. *First Principles*, i. 225.

|| One cubic inch of the gas contains about one fourth of a grain of metallic arsenic. H.

Exp. Soap bubbles blown with a mixture of this and oxygen gases, burn with a blue flame, a white smoke, and a strong alliaceous smell.

Exp. If detonated with about 4 volumes of oxygen, arsenious acid and water are formed. A stream of arsenuretted hydrogen gas, issuing from a bladder fitted with a stop-cock, and set on fire in a large receiver filled with oxygen, burns with a blue flame of uncommon splendour.

Action of alloy of potassium and arsenic.

1507. A solid compound of hydrogen and arsenic may be formed by acting on water with an alloy of potassium and arsenic; and, of course, much less hydrogen gas is evolved, than the same weight of uncombined potassium would liberate from water. It is described by Gay-Lussac, as separating in chestnut-brown coloured flocks. There appears, indeed, to be a strong affinity between hydrogen and arsenic; for Berzelius found that the recently prepared metal, when distilled along with oxide of tin, gave a drop or two of water. It must, therefore, have yielded hydrogen to the oxygen of the oxide. H. 2. 56.

Action of chlorine.

1508. If bubbles of chlorine be passed up into a jar of arsenuretted hydrogen, standing over warm water, flame and explosion are often produced, muriatic acid is formed, and a brown hydruret is deposited; but if the gas be passed in the same way by successive bubbles into chlorine, no inflammation results, absorption takes place, and muriatic acid and chloride of arsenic are formed. If the chlorine be not very pure, and when the gases are cold, inflammation seldom follows their mixture.

1509. Chlorine added to a mixture of sulphuretted with arsenuretted hydrogen, causes a deposit of red sulphuret of arsenic.

Action of nitric acid.

1510. Nitric acid suddenly decomposes arsenuretted hydrogen; water, oxide of arsenic, nitrous acid, and nitric oxide are the results.

Sulphuret.

1511. *Arsenic and Sulphur*.—By slowly fusing a mixture of metallic arsenic and sulphur, a *red sulphuret of arsenic* is obtained. It is crystallizable and of a vitreous fracture: its specific gravity is 3.4. It is usually known under the name of *realgar*, and occurs *native* in Germany and Switzerland, in veins of primitive rocks and among volcanic matter.

Orpiment.

1512. If white arsenic be dissolved in muriatic acid, and precipitated by hydrosulphuret of ammonia, a fine yellow sulphuret of arsenic falls, usually called *orpiment*.

Native.

1513. *Native Orpiment* is of a bright lemon, or golden colour. It is generally massive and lamellar. It occurs both in primitive and secondary rocks, in Suabia, Hungary, China, and South America.

Uses.

Orpiment is employed in calico-printing to de-oxygenate indigo, which thus becomes capable of attaching itself to the cloth. M. Braconnot recommends realgar for dyeing wool, silk, or cotton, of a fine yellow colour. Having mixed one part of sulphur, 2 parts of white arsenic, and 5 of potash of commerce, melt them in a crucible at a heat near that of redness. The yellow mass thus obtained is to be dissolved in hot

water, and filtered. It is then to be diluted, and sulphuric acid poured into it, of such strength as to produce a fleecy precipitate of a superb yellow colour. This dissolves with facility in ammonia, and gives a yellowish liquor, into which is to be poured an excess of ammonia for the purpose of discolouring it entirely. Goods plunged into this solution come out colourless, care being taken that no metallic vessels are used; but they assume a fine yellow as the ammonia evaporates. The colour is durable, and resists acids but not alkalies.*

1514. Realgar, which is the protosulphuret, is composed of 38 parts or 1 atom of metallic arsenic, and 16 or 1 atom of sulphur. Orpiment consists of 38 parts or 1 atom of arsenic, and 24 parts or an atom and a half of sulphur. It is therefore a *sesqui-sulphuret*. Composition.

1515. Sulphuric acid is slowly decomposed when boiled upon arsenic. Sulphurous acid is evolved, and difficultly soluble crystalline grains of *sulphate of arsenic* are deposited as the solution cools.† Sulphate.

1516. Arsenic forms alloys with most of the metals, and they are generally brittle. With potassium it forms a brownish compound, which, when put into water, evolves less hydrogen than pure potassium, in consequence of the formation of hydru-ret of arsenic. (1505.) With sodium, the alloy is either brown and of an earthy aspect, or grey and metallic, according to the proportions of the metals: water acts upon it as upon the former.‡ The alloy of arsenic and manganese is not known. With iron, zinc, and tin, it forms white brittle compounds; with copper it forms a white malleable alloy; with lead, a brittle compound of lamellar texture; with antimony, the alloy is brittle, hard, and very fusible. It combines with bismuth and probably with cobalt; but these alloys have not been examined. Alloys.

1517. Arsenic is used in a variety of the arts. It enters into metallic combinations, wherein a white colour is required. Glass manufacturers use it; but its effect on the composition of glass does not seem to be clearly explained. U. 179. Uses.

1518. The separation of arsenic from other metals may generally be accomplished by deflagration with nitre, by which it is acidified, and the arseniate of potassa may afterwards be washed out by hot water.

1519. As arsenic, either accidentally or intentionally taken, is a very frequent cause of death, and often the subject of judicial inquiry, it becomes of importance to point out the most effectual modes of discovering its presence. Where arsenic proves fatal, it is very seldom found in the contents of the stomach after death, but is generally previously voided by Methods of detecting arsenic.

* *Ann. de Chim. et Phys.* xii. 98.

† *Phosphuret of Arsenic* is formed by heating the metal, or its oxide, with phosphorus; it is grey and brittle. Neither the *Hypophosphite* nor *Phosphite of Arsenic* have been examined. *Phosphate of Arsenic* is formed in difficultly soluble crystalline grains, by boiling white arsenic in phosphoric acid.

‡ Gay-Lussac, and Thenard, *Recherches Physico-Chimiques*, Tom. 1.

vomiting or by stool; and we often can detect it in the matter thrown off the stomach, in the form of a white powder, subsiding in water. The inflammation of stomach which results is generally a secondary effect, and takes place equally, whether the poison be swallowed or applied to a wound.*

If minute quantities of white powder be detected, however, in the stomach after death, or in the matter vomited, it is to be carefully collected, and treated as follows:

Concentrate by heat in a capsule the suspected poisonous solution, having previously filtered it if necessary. Indeed, if it be very much disguised with animal or vegetable matters, it is better first of all to evaporate to dryness, and by a few drops of nitric acid to dissipate the organic products. The clear liquid being now placed in the middle of a bit of glass, lines are to be drawn out from it in different directions. To one of these a particle of weak ammoniacal water being applied, weak nitrate of silver may then be brushed over it with a hair pencil. By placing the glass, in different lights, either over white paper or obliquely before the eye, the slightest change of tint will be perceived. Ammoniaco-acetate of copper should be applied to another filament of the drop, deut-acetate of iron to a third, weak ammoniaco-acetate of cobalt to a fourth, sulphuretted water to a fifth, lime-water to a sixth, a drop of violet syrup to a seventh, and two galvanic wires at the opposite edges of the whole.† Thus with one single drop of solution, many exact experiments may be performed.

But the chief, the decisive trial remains, which is to take a little of the dry matter, mix it with a small pinch of dry black flux, put it into a narrow glass tube sealed at one end, and after cleansing its sides with a feather, urge its bottom with a blow-pipe till it be distinctly red-hot for a minute. Then garlic fumes will be smelt, and a steel-lustred coating of metallic arsenic will be seen in the tube about one-fourth of an inch above its bottom. Cut the tube across at that point by means of a fine file, detach the scale of arsenic with the point of a pen-knife, put a fragment of it into the bottom of a small wine-glass along with a few drops of ammoniaco-acetate of copper and triturate them well together for a few minutes with a round-headed glass rod. The mazarine blue colour will soon be transmuted into a lively grass-green, while the metallic scale will vanish. Thus we distinguish perfectly between a particle of metallic arsenic and one of animalized charcoal. Another particle of the scale may be placed between two smooth and bright

* Late investigations have shown that arsenic possesses the property of preserving from decay the bodies of those poisoned with it. The antiseptic effects sometimes extend only to the stomach and intestines, that is, to the parts directly in contact with it; but in some instances the whole body is preserved. The stomach and intestines of persons killed with arsenic have been found entire and firm at the distance of five, six, and fourteen months, or even at two years and a half after death; and in some of these instances the poison itself was detected. *Edin. Philos. Jour.* vii. 381.

† A voltaic battery made to act on a little arsenious solution placed on a bit of glass, develops metallic arsenic at the negative pole, and if this wire be copper, it will be whitened like tombac.

surfaces of copper, with a touch of fine oil; and whilst they are firmly pressed together, exposed to a red-heat. The tombac alloy will appear as a white stain. A third particle may be placed on a bit of heated metal, and held a little under the nostrils, when the garlic odour will be recognized. No danger can be apprehended, as the fragment need not exceed the tenth of a grain.

1520. It is to be observed that one or two of the precipitation tests may be equivocal from admixtures of various substances. Thus tincture of ginger gives with the cupreous reagent a green precipitate: and Dr Ure was at first led to suspect from that appearance, that an empirical tincture, put into his hands for examination, did contain arsenic. But a careful analysis satisfied him of its genuineness. Tea covers arsenic from the cupreous test. Such poisoned tea becomes by its addition of an obscure olive or violet red, but yields scarcely any precipitate. Sulphuretted hydrogen, however, throws down a fine yellow sulphuret of arsenic.*

1521. M. Orfila has gone into ample details on the modifications produced by wine, coffee, tea, broth, &c. on arsenical tests, of which a good tabular abstract is given in Mr Thomson's London Dispensary. But it is evident that the differences in these menstrua, as also in beers, are so great as to render precipitations and changes of colour by reagents very unsatisfactory witnesses, in a case of life and death. Hence the method of evaporation above described should never be neglected. Should the arsenic be combined with oil, the mixture ought to be boiled with water, and the oil then separated by the capillary action of wick-threads. If with resinous substances, these may be removed by oil of turpentine, not by alcohol, (as directed by Dr Black), which is a good solvent of arsenious acid. It may moreover be observed that both tea and coffee should be freed from their tannin by gelatin, which does not act on the arsenic previous to the use of reagents for the poison. When one part of arsenious acid in watery solution is added to ten parts of milk, the sulphuretted hydrogen present in the latter, occasions the white colour to pass into a canary yellow; the cupreous test gives it a slight green tint, and the nitrate of silver produces no visible change, though even more arsenic be added; but the hydro-sulphurets throw down a golden yellow, with the aid of a few drops of an acid. The liquid contained in the stomach of a rabbit poisoned with a solution of 3 grains of arsenious acid, afforded a white precipitate with nitrate of silver, greyish-white with lime-water, green with the ammoniaco-sulphate, and deep yellow with sulphuretted hydrogen-water. U. 18.†

* Both cadmium and arsenic are precipitated by sulphuretted hydrogen of a yellowish colour, but may be distinguished by employing hydro-sulphuret of ammonia, which gives no precipitate with arsenious acid, but forms one with cadmium. *Jour. de Pharm.* June, 1827.

† Dr Cooper recommends a solution of chromate of potassa as one of the best tests of arsenic. One drop is turned green by the fourth of a grain of arsenic, by two or three drops of Fowler's solution or any

SECTION XXV. *Molybdenum.*

Ores.

1522. THE sulphuret is the most common natural compound of this metal. When this ore, in fine powder, is digested in nitro-muriatic acid until completely decomposed, and the residue is briskly heated, in order to expel sulphuric acid, molybdic acid remains in the form of a white heavy powder. From this acid metallic molybdenum may be obtained by exposing it with charcoal to the strongest heat of a smith's forge; or by conducting over it a current of hydrogen gas while strongly heated in a tube of porcelain.*

Properties.

1523. Molybdenum is a brittle metal, very infusible, and of a white colour. It has been procured but in small quantities, and its properties are known imperfectly. Its specific gravity, according to Hielm, is 7.4, according to Bucholz, it is as high as 8.6.

Molybdenum
and oxygen.

1524. *Molybdenum and Oxygen.*—When heated in open vessels molybdenum absorbs oxygen, and is converted into *molybdic acid*, and the same compound is generated by the action of chlorine or nitro-muriatic acid. Molybdic acid, according to Bucholz, is composed of 48 parts of molybdenum and 24 parts of oxygen; and consequently on the supposition that this acid contains 3 atoms of oxygen, 48 is the atomic weight of the metal itself.

Molybdic
acid.

Properties.

It is a white powder, of specific gravity 3.4. It has a sharp metallic taste, reddens litmus paper, and forms salts with alkaline bases. It is very sparingly soluble in water; but the molybdates of potassa, soda, and ammonia dissolve in that fluid, and the molybdic acid is precipitated from the solutions by any of the strong acids.

Oxides.

1525. Berzelius has lately described the two oxides of molybdenum.† The *protoxide* is produced when we macerate the solution of a salt, with a base of the deutoxide, with mercury, and add, from time to time, a liquid amalgam of potas-

other arsenite of potassa. The arsenious acid takes oxygen from the chromic, which is converted into oxide of chrome. To exhibit the effect, take five watch glasses, put on one, two, or three drops of a watery solution of white arsenic; on the second, as much arsenite of potassa; on the third, one-fourth of a grain of white arsenic in substance; on the fourth, two or three drops of solution of corrosive sublimate; on the fifth, two or three drops of solution of copper. Add to each three or four drops of a solution of chromate of potassa. In half an hour a bright clean grass-green colour will appear in numbers 1, 2, 3, unchangeable by ammonia; number 4 will instantly exhibit an orange precipitate; and number 5 a green, which a drop of ammonia will instantly change to blue. *Amer. Journal of Science*, 4, 155.

The reader is referred for further particulars on this subject to *Henry's Elements of Chemistry*, vol. ii. p. 588, 10th edit.: to *Murray's System*, vol. iii. p. 441, 4th edit.: to *Dr Bostock's Paper*, in the *Edinb. Med. and Surg. Jour.* vol. v. p. 166: to *Mr Hume's Essay* in the *Phil. Mag.* vol. xxxiii.; and *London Med. and Phys. Journal*, vol. xxiii.: to *Dr Marcel's Paper*, in the *Medico-Chirurgical Transactions*, vol. ii.: to *Mr Sylvesters's Observations* in *Nicholson's Journal*, vol. xxxiii.: to *Beck's Medical Jurisprudence*, vol. ii.: to *Dr Traill's Paper*, in *Boston Journal of Philos.* 1543: *Edin. Medico-Chirurg. Trans.* vol. ii.

* Berzelius.

† *Edin. Philos. Jour.* iv. 133

sium.* The colour of the liquid becomes deeper, and ends by growing black. Before the introduction of the amalgam, muriatic acid must be added to prevent a part of the deutoxide from being precipitated before its entire reduction to the protoxide. The black solution is then precipitated by ammonia, and the black precipitate is the hydrate of the protoxide, which must be well washed, and then dried in *vacuo*. The hydrate then appears under the form of a jet black powder. When heated in *vacuo*, it slowly gives out its water, and afterwards at a temperature which approaches to that of brown red, it takes fire, and burns with scintillation. The anhydrous protoxide is insoluble in acids. When heated in air, it takes fire, and burns feebly, producing the brown oxide of molybdenum.

1526. The salts of this oxide are black, and their dilute solutions have a compound colour of green, black, and brown, though sometimes they assume a fine purple colour.

1527. *Deutoxide of Molybdenum* may be procured by Deutoxide. digesting a mixture of molybdic acid, metallic molybdenum, and sulphuric or muriatic acid, till the colour of the liquid becomes a deep red. Instead of metallic molybdenum, we may substitute metallic copper. The red liquid gives, with ammonia, a rust-yellow precipitate, which is the hydrate of the deutoxide; it is very soluble in water, and the saturated solution is red. It reddens turnsol. The hydrate dissolves in acids and gives salts, whose solutions are red, but which, when evaporated to dryness, are almost black.

1528. According to Berzelius, what has been called *molybdous acid* is a *bi-molybdate of the deutoxide of molybdenum*. Molybdous acid. It cannot be combined with alkalies, which, on the contrary, decompose it by precipitating the hydrate of the yellow oxide and combining with the molybdic acid. It may be produced most readily by dissolving the bi-molybdate of ammonia, and adding to it a solution of a salt with a base of the deutoxide. It produces a precipitate of a fine deep blue, which is very soluble in water, and is only deposited because the water contains salts. It may be washed with a solution of sal-ammoniac, afterwards removing the salt by a little cold water. It gives with warm water a blue solution, highly saturated, which may be preserved at the ordinary temperature of the atmosphere. In the dry form it resembles indigo, and retains its solubility in water.

1529. Berzelius has likewise formed three *chlorides of molybdenum*. Chlorides. The first is red, and a little volatile. The second is black, very fusible, very volatile, and crystallizes in a black mass of a brilliant colour, like iodine which it resembles even in the colour of its gas, which, however, is more red than violet. The third is colourless, and crystallizes in scales. These

* It may also be formed by using zinc in place of the amalgam, but the protoxide then retains the oxide of zinc in a very obstinate manner.

three chlorides correspond in composition to the compounds of this metal with oxygen.*

Sulphurets. 1530. Berzelius has lately discovered a new *sulphuret of molybdenum*, of a ruby red colour, transparent and crystallized. It is proportional to the molybdic acid; that is, it contains three atoms of sulphur to one of metal. It combines with the metallic proto-sulphurets, and forms with them particular salts, of which a great number are soluble in water.

SECTION XXVI. Chromium.

Discovery. 1531. Chromium† was discovered by Vauquelin in 1797‡ in a beautiful red mineral, the native chromate of lead. It has since been detected in the mineral called *chromate of iron*, a compound of the oxides of chromium and iron which occurs in several places in Europe and in this country.

How obtained. 1532. Chromium, which has been procured in very small quantity, owing to its powerful attraction for oxygen, may be obtained by exposing the oxide of chromium mixed with charcoal to the most intense heat of a smith's forge. It is a brittle metal, of a greyish white colour, and very infusible. Its specific gravity is 5.9.

Oxides. 1533. *Chromium and Oxygen*.—Chromium unites with oxygen in three proportions, forming two oxides and one acid. Dr Thomson has shown that the equivalent of chromic acid is 52, so that on the probable assumption of its being composed of 1 atom of chromium, and three atoms of oxygen, 28 must be the atomic weight of the metal. According to these data, the composition of the oxides and acid of chromium may be thus stated.

| | Metal. | Oxygen. |
|----------------------|--------------|---------------|
| Protoxide | 28 or 1 atom | 8 or 1 atom. |
| Deutoxide | 28 | 16 " 2 atoms. |
| Chromic acid | 28 | 24 " 3 " |

Protoxide. 1534. *Protoxide*.—This oxide is easily prepared by dissolving the chromate of potassa in water, and mixing it with a solution of the proto-nitrate of mercury, when an orange-coloured precipitate, the chromate of the protoxide of mercury, subsides. On heating this salt to redness in an earthen crucible, the mercury is dissipated in vapour, and the chromic acid is resolved into oxygen and the protoxide of chromium.

Properties. The protoxide of chromium is of a green colour, and suffers no change by heat. It is insoluble in water, and after being strongly heated, resists the action of the most powerful acids.

* Iodine does not combine in the dry way with molybdenum, but hydriodic acid dissolves the protoxide and the deutoxide. The molybdic acid decomposes it, and separates the iodine from it. *Edin. Philos. Jour.* iv.

† From *Xsappu*, colour, indicative of its remarkable tendency to form coloured compounds:

‡ *Ann. de Chim.* xxv. and lxx.

Deflagrated with nitre, it is oxidized to its maximum, and is thus reconverted into chromic acid. Fused with borax or vitreous substances, it communicates to them a beautiful green colour, a property which affords an excellent test of its presence, and renders it exceedingly useful in the arts.

1535. The protoxide of chromium is a salifiable base, and its salts, which have a green colour, may be easily prepared in the following manner.

To a boiling solution of the chromate of potassa in water, equal measures of strong muriatic acid and alcohol are added in successive small portions, until the red tint of the chromic acid disappears entirely, and the liquid acquires a pure green colour. On pouring an excess of pure ammonia into this solution, a pale green bulky precipitate is formed, which consists of 1 atom of the protoxide and 26 atoms of water.* The hydrate is readily dissolved by acids.

1536. The brown or *deutoxide* of chromium is formed by Deutoxide. exposing the nitrate of the protoxide to a temperature precisely sufficient for decomposing the nitric acid. This compound is considered by M. Mans as a combination of the protoxide of chromium and chromic acid.† T. 402.

1537. *Peroxide of Chromium* or *chromic acid* is most easily Peroxide. procured by the decomposition of the native chromate of lead. The ore reduced to powder, is boiled with twice its weight of carbonate of potassa. An orange-coloured solution, composed of potassa and chromic acid, is thus formed, to which sulphuric acid is to be added. On evaporation, crystals of chromic acid are formed, along with the sulphate of potassa. Or the acid may be obtained by adding nitrate of baryta to the chromate of potassa and subsequently decomposing the chromate of baryta which falls, by sulphuric acid.

Chromate of iron, however, from the great plenty in which it is found, is a much cheaper source of chromic acid. After reducing it to fine powder, it is to be mixed with half its weight of nitrate of potassa, and heated strongly for an hour or two in a crucible. The mass is to be repeatedly digested with water, and the coloured liquids, which are slightly alkaline, saturated with nitric acid, and concentrated by evaporation, till no more crystals of nitre can be obtained from them. The yellow liquid being now set aside for a week or two, deposits a copious crop of yellow crystals in small needles. These are to be separated, dissolved in water, and crystallized over again. They are then sufficiently pure chromate of potassa. From the solution of these crystals, or indeed from the yellow liquid, nitrate of mercury throws down a red powder, which is chromate of mercury. When sufficiently heated, this compound is decomposed, and yields chromic acid or chromic oxide, from either of which metallic chromium may be obtained by heating it violently with charcoal in a crucible. H. 2. 62.‡

1538. Chromic acid is of a red colour; its taste is sour and Properties. metallic, and it may be obtained from its aqueous solutions in prismatic crystals, of a ruby colour. When heated red hot, it gives out a portion of oxygen, and becomes the green protoxide; it imparts colour to the ruby.

1539. *Fluo-chromic acid gas*.—When a mixture of fluor Fluo chromic acid gas. spar and chromate of lead is distilled with fuming or even common sulphuric acid in a leaden retort, a red-coloured gas is

* Thomson.

† See *Quart. Jour.* v. N. S. 226.

‡ For a new process, see Brewster's *Jour.* xvii. 175.

disengaged, which is composed of fluoric and chromic acids. This gas acts rapidly on glass, with deposition of chromic acid and formation of fluo-silicic acid gas. It is absorbed by water, and the solution is found to contain a mixture of fluoric and chromic acids. The watery vapour of the air effects its decomposition, so that when mixed with air, red fumes appear, owing to the separation of minute crystals of chromic acid.

This gas may be regarded as a compound of fluorine and chromium.

Chloro-chromic acid gas.

1540. *Chloro-chromic acid gas*.—This compound is formed by the action of fuming sulphuric acid on a mixture of chromate of lead and chloride of sodium. It is a red coloured gas which may be collected in glass vessels over mercury. It is decomposed instantly by water, and yields a solution of muriatic and chromic acids. It may be regarded either as a compound of muriatic and chromic acids, or of chlorine and chromium.*

Chromate of potassa.

1541. *Chromate of Potassa* forms crystals the primary shape of which is a right rhombic prism.† Their colour is an intense lemon yellow, with a slight shade of orange. The colouring power of this salt is so great that 1 grain in 40,000 grains of water forms a solution which is perceptibly yellow. Its taste is cooling, bitter, and very disagreeable, remaining long in the mouth. One hundred parts of water at 60° dissolve about 48 parts, but boiling water dissolves almost any quantity. It is insoluble in alcohol. Its solution in water decomposes most of the metallic salts; those of lead of a beautiful yellow colour, now much used as a pigment; those of mercury of a fine red; copper and iron reddish brown; silver, dark red. According to Dr Thomson, chromate of potassa is composed of

| | |
|----------------------------------|-------|
| 1 atom of chromic acid | = 52 |
| 1 do. of potassa | = 48 |
| | <hr/> |
| | 100 |

Bi-chromate.

1542. *Bi-chromate of Potassa*.—When to a solution of these crystals in water, such a quantity of sulphuric acid is added, as to give the liquor a sour taste, and it is set aside for 24 hours, small regular needles are deposited; or sometimes rectangular tables of considerable size, and of a beautiful orange red colour. These crystals‡ are the *bi-chromate of potassa*. They are much less soluble in water than the chromate; for 100 parts at 60° Fahr. dissolve only about 10 parts. The solution has an intense orange colour, and reddens vegetable blues. This salt is composed of

| | |
|---|----------------|
| 2 atoms of chromic acid = 104 | 63,421 |
| 1 atom of potassa . . = 48 | 31,579 |
| | <hr/> |
| 152 | 100. H. 2. 64. |

* These gases were discovered by M. Unverdorben.—*Edin. Jour. of Science*, No. vii.

† *Ann. of Philos.* vi. 120.

‡ Figured by Mr Levy, in *Quart. Jour.* xv. 287.

1543. The chromates of ammonia, soda, lime, and magnesia are soluble and crystallizable, and of an orange colour. The chromates of baryta and strontia are difficultly soluble, and may be formed by adding chromate of potassa or soda to their soluble saline compounds. The other insoluble metallic chromates may be formed in the same way, and their colours, which are various and beautiful, often enable us to judge of the nature of the metal present. Thus chromate of soda forms insoluble precipitates in solutions of silver, mercury, lead, copper, iron and uranium; the colours are crimson, red, orange or yellow, apple-green, brown, and yellow. It forms no precipitate in solutions of nickel, zinc, tin, cobalt, gold, or platinum; whence perhaps, it may be inferred, that the chromates of the latter metals are soluble. The reddish brown chromate of copper which is precipitated from sulphate of copper by chromate of potassa, is soluble in dilute ammonia forming a clear solution of a deep green colour.*

Characters of the chromates of ammonia and soda, &c.

The chromates are decomposed by muriatic, nitric, and sulphuric acids. Muriatic acid, heated with the chromates, evolves chlorine, the chromic acid being reduced to the state of oxide.†

Action of acids.

1544. The principal use to which chromium has been applied, is the preparation of the beautiful pigment, chromate of lead, known in commerce by the name of *chrome yellow*. It is prepared by mixing the solutions of chromate of potassa and nitrate or acetate of lead. Nineteen parts of bi-chromate of potassa decompose 41,5 of dry nitrate of lead. The insoluble chromate of lead consists of 1 atom of chromic acid + 1 atom of protoxide of lead.‡

Uses:

1545. The *chromate of lead* is found native. It is of a rich yellow colour, and is employed in the arts of painting and dyeing. A *di-chromate* of lead, composed of 1 atom of chromic acid and 2 atoms of the protoxide of lead, may be formed by boiling carbonate of lead with an excess of chromate of potassa. It is of a beautiful red colour, and has been recommended by Mr Badams as a pigment.§

Chromate of lead.

It appears probable, also, from the experiments of Lassaigne,|| that chromium admits of being successfully applied to the arts of dyeing and calico-printing; and in the latter very striking effects have already been produced on the large scale. H. The green oxide of chromium is occasionally used in porcelain and enamel painting.

SECTION XXVII. Tungsten.

1546. Tungsten, or Tungstenum, signifies a heavy stone, and is a name given by the Swedes to a mineral, which Scheele

Origin of the name.

* *Quart. Jour.* xix.

† The most correct details respecting the chromates that have been published are to be found in Vauquelin's *Essay Annales de Chimie*, lxx.

‡ Thomson.

§ *Boston Jour. of Philos.* iii. 45.

|| *Ann. de Chim. et Phys.* xiv. 299, xv. 76, and xvi. 400.

found to contain a peculiar metal, as he supposed in the state of an acid, united with lime. The same metallic substance was afterwards found by Don d'Elhuyarts united with iron and manganese in wolfram.*

Properties.

1547. The metal is obtained by exposing a mixture of tungstic acid and charcoal to a strong heat. It is difficult of fusion, very hard, brittle, and of an iron colour. Its specific gravity is 17,5. By the action of heat and air, tungsten is converted into an oxide which is of a yellow colour. It has been called by some *Scheelium*, by others *wolframium*.

Wolfram,

Wolfram is found in primitive countries generally accompanying tin ores; its colour is brownish black; it occurs massive and crystallized, its primitive form being a rectangular parallel-opiped. It abounds in Cornwall.

decomposition of.

It may be decomposed by ignition with three times its weight of nitre; the fused mass, digested in boiling water and filtered, furnishes a solution, which upon the addition of muriatic acid, gives a precipitate regarded by Scheele as tungstic acid, but which in fact is a compound of muriatic and tungstic acids and potassa. Dissolve this in boiling carbonate of potassa, precipitate by muriatic acid, wash the precipitate, and digest it in nitric acid. Then wash and dry it, and it is pure tungstic acid.†

Tungstate of lime.

1548 *Native Tungstate of Lime* is a whitish semi-transparent substance, found in England, Saxony, Bohemia, and Sweden, and occurring crystallized and massive. Its most usual form is the octoëdron. It may be decomposed by fusion with four parts of carbonate of potassa, the fused mass is digested in about twelve parts of boiling water, and filtered. Nitric acid precipitates the peroxide.

Tungstate of lime was found by Klaproth to consist of 77,75 acid + 22,25 lime; but Berzelius states its components to be 80,4 acid + 19,6 base.

Oxides

1549. There are two oxides of tungsten, the brown, and the yellow or *tungstic acid*.

1550. The brown oxide is formed by transmitting hydrogen gas over tungstic acid in an ignited glass tube. It takes fire when heated in the air, and burns like tinder, passing into tungstic acid.

M. Wöhler's process for obtaining tungstic acid.

It had been remarked by M. Wöhler, that when a mixture of tungsten, potassa, and muriate of ammonia, is heated together the tungstic acid is reduced by the hydrogen of the ammonia to an oxide, which separates when the mass is dissolved in water. This property he has applied to the preparation of tungstic acid in the following manner. A mixture of powdered wolfram and carbonate of potassa is fused; the tungstate of potassa is dissolved in water, and a sufficient quantity of muriate of ammonia then added. The liquor is evaporated to dryness, and the mass fused in a Hessian crucible, till the muriate of ammonia is entirely decomposed and evaporated. By dissolving the fluid mass in water, a black powder separates, which

* *Ann. de Chim. et Phys.* iii. 161.

† Bucholz, as quoted by Thomson, *System*, ii. 122.

is oxide of tungsten. This is boiled with a weak solution of potassa, to remove a small quantity of acid and difficultly soluble tungstate of potassa, and then washed with abundance of distilled water. This oxide when heated in an open crucible, burns vividly, and is changed into a yellow powder, which is tungstic acid. H. 2. 696.

1551. *Tungstic Acid*, or *Peroxide of Tungsten*, is tasteless and insoluble in water; its specific gravity is 6. When violently heated, it becomes green, grey, and black, probably from the loss of oxygen. It combines with several of the metallic oxides, and with alkaline bases forming salts called *tungstates*. It was found by Guyton to give considerable permanence to vegetable colours; hence it probably might prove useful in the art of dyeing were it more abundantly procurable. It is composed, according to Bucholz of 80 tungsten and 20 oxygen,* supposing the acid to consist of an atom of metal and 3 atoms of oxygen this would give 96 for the equivalent of tungsten, and 120 for that of tungstic acid. H. 2. 66.

1552. *Tungsten and Chlorine*.—Sir H. Davy found that metallic tungsten burns with a deep red light when heated in chlorine, and produces a white substance which is decomposed by the action of water, into tungstic and muriatic acids. M. Wöhler† has shown the existence of three compounds of chlorine and tungsten.

When metallic tungsten is heated in chlorine, it takes fire and burns into a chloride, with a minimum of chlorine. The compound appears sometimes as delicate fine needles, of a deep red colour resembling wool, but more frequently as a fused deep red compact mass, with the brilliant fracture of cinnabar. When heated, it fuses, boils, and yields a red vapour. In water it gradually decomposes, producing muriatic acid and oxide of tungsten. This compound dissolves in solution of pure potassa, evolving hydrogen, forming chloride of potassium, and tungstate of potassa. Similar effects take place in ammonia.

1553. When the black oxide is heated in chlorine in a tube, combustion takes place, dense fumes are formed, which ultimately produce a thick sublimate of white scales, resembling in appearance native boracic acid; this is the *perchloride of tungsten*. In the air it gradually becomes tungstic and muriatic acids: the change is more rapid in water. It is volatile at a low temperature, without previously fusing. Heated on platinum foil it is also decomposed into muriatic and tungstic acid.

1554. The third compound, on the composition of which no experiment has been made, is generally formed at the same time with the perchloride, but in small quantity. It has been obtained by heating the sulphuret of tungsten in chlorine. This is the most beautiful compound of all, existing in long transparent crystals, of a fine red colour; it readily fuses, and on

* Thenard, *Traite*, 2. 400 edit. 4. U. 114.

† *Ann. de Chim.* 29. 43.—*Philos. Mag.* 66. 263.

cooling crystallizes in long needles. It is volatile, and instantly changes in contact with the air into tungstic acid. Thrown into water it swells like caustic lime, disengages heat, a slight noise is heard, and it is instantly changed into tungstic acid.*

Sulphuret.

1555. Berzelius has lately examined the *sulphuret of tungsten*, with the view of determining the capacity of saturation of the metal. He heated together one part of powdered tungstic acid, and four of sulphuret of mercury. The latter metal was expelled and a blackish grey compound remained, not unlike sulphuret of copper. On analysis it afforded

| | | | | | | Atoms. |
|----------|-------|--------|-------|-------|-------|--------|
| Tungsten | . . . | 74,891 | . . . | 100 | . . . | 1 = 96 |
| Sulphur | . . . | 25,109 | . . . | 35,53 | . . . | 2 = 34 |
| | | | | 100, | | 130 |

One hundred parts of the sulphuret, calcined so as to expel the sulphur and oxidize the metal, gave 93,5 of tungstic acid; and as that quantity of acid must contain 74,891 metal, 100 should contain 80,09, which agrees with the experiment of Bucholz. It may be remarked, that the sulphur in the sulphuret is rather more than double the oxygen in the new oxide obtained by Berzelius, but the difference is not greater than may be accounted for by the unavoidable errors of the experiments. Consisting of two atoms of sulphur and one of metal, it is in fact to be considered as a bi-sulphuret of tungsten. H. 2. 67.

Some of the tungstates have been examined by Scheele, and others by Vauquelin and Hecht,† but their history remains very imperfect.‡

SECTION XXVIII. Columbium.

Discovery.

1556. This metal was discovered in 1801, by Mr Hatchett, in a black mineral in the British museum, which had been sent by Gov. Winthrop to Sir Hans Sloane, from the vicinity of New-London in Connecticut.

* M. Wöhler.

† *Journal des Mines*, N. 19.Tungstate
of potassa,

— of soda,

— of lime,

— of magne-
sia.— of manga-
nese, &c.

‡ *Tungstate of Ammonia* is procured in crystalline scales, of a metallic taste, by digesting the acid in ammonia or its carbonate. It contains, according to Vauquelin, 78 of acid, and 22 ammonia and water. *Tungstate of Potassa* is uncrystallizable and deliquescent. The acids occasion precipitates in its solution, which are triple compounds of tungstic acid, potassa, and the acid used as precipitant. The *Nitrotungstate of Potassa* is the salt originally described by Scheele as tungstic acid. It dissolves in 20 parts of water, at 212°, and reddens litmus. *Tungstate of Soda* crystallizes in hexaëdral tables, soluble in 4 of cold, and 2 parts of boiling water, and of an acid taste. Sulphuric, nitric, and muriatic acids occasion precipitates, as in the tungstate of potassa. *Tungstate of Lime*, of *Baryta*, and of *Strontia*, are insoluble white compounds. *Tungstate of Magnesia* is obtained by boiling the acid with magnesia, filtering, and evaporating; it crystallizes in pearly scales. The acids produce precipitates of triple compounds in its solution. *Tungstate of Manganese*, formed by adding tungstate of potassa to muriate of manganese, is an insoluble white powder. § *Tungstate of Iron* is also insoluble: *Tungstate of Zinc* and of *Tin* have not been examined, nor have any of the remaining tungstates been examined in their pure state.

§ John, Gehlen's *Journal*, iv.

By alternate fusion with potassa, and digestion in muriatic acid, the mineral was decomposed; the acid combining with oxide of iron, and the alkali with a peculiar metallic acid, separable by the addition of diluted nitric acid, which threw down a copious white sediment.

1557. A metal analogous in its properties to columbium, was discovered by Mr Ekeberg, a Swedish chemist, in two different fossils, called Tantalite and Ytthro-tantalite. To this metal he gave the name of *tantalum*.*

Tantalite and ytthro-tantalite.

1558. Columbium may be procured from columbite or tantalite, by the following process:

Process for obtaining columbium.

Mix five parts of the finely powdered mineral with 25 of carbonate of potassa, and 10 of borax; fuse the mixture, and when cold digest it in muriatic acid; this dissolves every thing except the oxide of columbium, which remains in the form of a white powder.† From 5 grains of columbite, Dr Wollaston obtained

| | |
|--------------------|---------------|
| Oxide of columbium | 4 grains |
| — iron . . | $\frac{3}{4}$ |
| — manganese | $\frac{1}{4}$ |

From 5 grains of tantalite he procured

| | |
|--------------------|-----------------------|
| Oxide of columbium | $4\frac{1}{4}$ grains |
| — iron . . | $\frac{1}{2}$ |
| — manganese | $\frac{2}{10}$ |

1559. Berzelius is the only person who has obtained metallic columbium. His method consisted in introducing the oxide, which had previously been strongly heated, into a cavity about one inch and a half deep and of the diameter of a goose-quill, artificially formed in a piece of charcoal. To this cavity a stopper of charcoal was fitted, and the whole closed in a Hessian crucible was exposed to a violent fire during an hour.

Berzelius' method.

He has more lately obtained columbium, by acting with potassium on the fluo-tantalate of potassa. The mixture when heated enters into ignition, fluat of potassa is formed, and may be separated by water from the revived columbium. The colour of the metal is perfectly black, but when dried it takes a polish by friction and becomes of an iron-grey colour. It is an extremely bad conductor of electricity. It is not attacked by nitric or muriatic acid separately applied, and in a very slight degree by nitro-muriatic acid. Sulphuric acid has no action on it, even at a boiling heat, or when mixed with nitric acid. Fluoric acid dissolves it with an extrication of hydrogen gas, and the mixture becomes hot.

Properties of the metal.

1560. The characters of *white oxide of columbium* are very well marked. It is nearly insoluble in muriatic, nitric, and sulphuric acids; it is very soluble in potassa, and carbonate of potassa; 8 grains of the latter, fused with one of the oxide render it soluble in water. It is much less soluble in soda, and only retained while hot. From the readiness with which this oxide combines with potassa Mr Hatchett called it *columbic acid*.

White oxide.

* The identity of these metals was established in 1809 by Dr Wollaston.

† Wollaston *Phil. Trans.* 1809, p. 248.

Action of
heat.

1561. When the metal is heated it catches fire before becoming red-hot, and burns vividly, at the same time that it is converted into columbic acid; but as several circumstances prevent the increase of weight from being accurately determined, Berzelius investigated the composition of the acid, by acting on the sulphuret, artificially prepared. In this way he ascertained the composition of columbic acid to be

| | |
|-------------------|------------------|
| Columbium | 88,487 or 100 |
| Oxygen | 11,513 " 13,011. |

Precipitated from muriatic acid by potassa, and dried at a gentle heat, columbic acid forms a hydrate consisting of

| | |
|-----------------------|-------|
| Columbic acid | 88,83 |
| Water | 11,17 |

And the oxide containing two-thirds of the oxygen in the acid, is composed of

| | |
|-------------------|----------------|
| Columbium | 12,019 or 100 |
| Oxygen | 7,781 " 8,674* |

Columbate of
potassa.

1562. *Columbate of Potassa*, as appears from Mr Hatchett's experiments, forms white glittering scales, like boracic acid. Acids precipitate the columbic acid from this solution.

Test.

1563. Infusion of galls, added to the solution of columbate of potassa produces a very characteristic orange-coloured precipitate. Neither ferro-cyanate of potassa, nor hydro-sulphurets, occasion any change.

Peculiar
character.

There is a character very peculiar to the oxide of columbium, which is its ready solubility in tartaric, citric, and oxalic acids. In all these cases the newly precipitated oxide must be used, for when dried, it becomes very intractable.

SECTION XXIX. Nickel.

Ores.

1564. Nickel is found native, and is a constituent of meteoric iron. It occurs likewise in the copper-coloured mineral of Westphalia, termed *copper nickel*, a native arseniuret of nickel, which, in addition to its chief constituents, contains sulphur, iron, cobalt, and copper. From this mineral the oxalate of nickel may be prepared by a process similar to that for forming the oxalate of cobalt. (1427)†

Metallic nickel,
how obtained.

1565. Metallic nickel which may be prepared either by heating the oxalate in close vessels, or by the combined action of heat and charcoal or hydrogen on the oxide of nickel, is of a white colour, intermediate between that of tin and silver.

* *Ann. de Chim. et de Phys.* xxix. 303.

† For an account of other methods of obtaining pure nickel, see Henry's *Chem.* 2, 169; and *Quart. Jour.* 44, 396. On the separation of arsenic from nickel, see *Quart. Jour.* N. S. iii. 209.

1566. Dr Clarke, of Cambridge, (Eng.) has shown that crystals of nitrate of nickel, when placed in a cavity scooped out of a piece of charcoal, and exposed to the oxy-hydrogen blow-pipe, afford a bead of metallic nickel. This, however, is a process obviously adapted to yield only very minute quantities of nickel.* H. 2. 170.

1567. Nickel acts upon the magnetic needle, and is itself capable of becoming a magnet. It is difficultly fusible, but absorbs oxygen readily when heated red-hot. It is malleable, and its specific gravity is about 8,5. Properties.

1568. Nickel appears to be susceptible of two different states of oxidation. By long exposure to a red heat, with free access of air, it is converted into a dark brown oxide, which is still magnetic. In oxygen gas it burns vividly, and throws out sparks. When precipitated from its solution by alkalies, and moderately ignited, it becomes of an ash-grey colour with a slight tinge of blue or green, and in this state consists, according to Klaproth, of 100 metal + 51,5 oxygen. By farther ignition, it becomes blackish grey, and then consists, according to Richter, of 100 metal and 28,2 oxygen. The composition of the oxides is stated very differently by different chemists. According to Lassaigne, the oxide obtained by gently calcining nitrate of iron consists of Oxides.

| | | | | | | | | |
|--------|-------|-------|-------|-----|-------|----------|-----|---|
| Nickel | . . . | 83,34 | . . . | 100 | . . . | 1 atom = | 40 | Composition: |
| Oxygen | . . . | 16,66 | . . . | 20 | . . . | 1 " | = 8 | |
| | | | | 100 | | | 48 | |

Dr Thomson, from the composition of the sulphate, derives 26 for the atomic weight of nickel, and 34 for that of the protoxide. Mr Phillips considers 29 and Mr Brande 30 as the equivalent of the metal.

1569. Thenard describes a black *peroxide* of nickel, obtained by passing a current of chlorine gas through water in which the hydrate is suspended. It evolves chlorine from muriatic acid, and has several analogies with oxide of manganese. In a sufficiently high temperature, these oxides are reducible without addition, nor is nickel more tarnished by a strong heat than gold, silver, or platinum. H. 2. 172 Peroxide.

1570. *Nickel and Chlorine.*—When nickel is heated in chlorine gas, an olive-coloured compound is obtained, which is probably the *bi-chloride*. The *proto-chloride* is obtained by evaporating and strongly heating the muriate: it forms brilliant yellow scales. Chloride.

1571. *Iodide of Nickel* may be formed by adding solution of hydriodate of potassa to sulphate or nitrate of nickel; it is of a green colour, and insoluble. Iodide.

1572. The appropriate solvents of nickel are the nitric and nitro-muriatic acids. The nitric solution has a beautiful grass- Action of nitric and nitro-muriatic acid.

* *Ann. of Philos.* xiv. p. 142.
52

green colour, and on evaporation affords rhomboidal crystals. Carbonate of potassa throws down an apple-green precipitate, which assumes a dark grey colour when heated. The fixed alkalis occasion a bulky greenish white precipitate, which is a hydrate or hydro-oxide of nickel, composed of 76 per cent. of the protoxide and 24 water.

Action of
Ammonia.

When pure ammonia is added to nitrate of nickel a precipitate is formed, resembling that which is separated by ammonia from a solution of copper, but not of so deep a hue. This colour changes, in an hour or two, to an amethyst red, and to a violet; which colours are converted to apple-green by an acid, and again to blue and violet by ammonia. If the precipitate retain its blue colour, the presence of copper is indicated.* This precipitate, which is a hydrate, is redissolved by an excess of ammonia; and by this property the oxide of nickel may be separated, in analysis, from those of almost all other metals.

Sulphuret.

1573. *Sulphuret of Nickel.* Solutions of all the salts of nickel are decomposed by alkaline hydro-sulphurets, with which they form black precipitates; but sulphuretted hydrogen has no effect on them. Nickel may, however, be combined directly with sulphur by fusion, and forms a grey compound with a metallic lustre.

The *proto-sulphuret* contains 34 per cent. of sulphur; and the *bi-sulphuret*, which may be formed by heating the protoxide with sulphur, contains 43,5 per cent. of sulphur.†

Sulphate.

1574. *Sulphate of Nickel* is formed by digesting the oxide in dilute sulphuric acid. A bright green solution is formed, which affords quadrangular prismatic crystals, soluble in about 3 parts of water at 60°. Their taste is sweet and astringent. This salt is also obtained by heating common nickel in sulphuric acid with the occasional addition of nitric acid.

According to Dr Thomson‡ this salt consists of

| | | | | | |
|--------------------------|------|----|---------|---|----|
| Sulphuric acid | 29,2 | or | 1 atom | = | 40 |
| Protoxide | 24,8 | " | 1 " | = | 34 |
| Water | 46,0 | " | 7 atoms | = | 63 |

From which he deduces the equivalent number of nickel 3,25 = 26, oxygen being considered as 8.

Union with
carbon.

1575. *Nickel and Carbon.*—Nickel is susceptible of uniting with carbon, and is apt indeed to form this union when reduced from its salts by carbonaceous matter. According to Mr Ross, it composes a substance resembling iodine or micaceous iron ore.§||

Carbonate.

1576. *Carbonate of Nickel* is precipitated in the form of a green powder, when carbonate of potassa is added to sulphate

* Richter, in *Nicholson's Journal*, xii.

† Mr E. Davy.

‡ *First Prin.* ii. 133.

§ *Ann. of Philos.* N. S. ii. 62, 149, and iii. 201.

|| *Phosphate of Nickel* being nearly insoluble, is precipitated upon adding phosphate of soda to a solution of nickel. It is of a pale green colour.

of nickel. It is probably a compound of 1 proportional of each of its components.*

1577. Ferro-cyanate of potassa occasions a very characteristic pale grey precipitate in dilute solutions of nickel: in concentrated solutions the precipitate is pale green.

1578. Arseniate of potassa, dropped into nitrate of nickel occasions the precipitation of a pale green *arseniate of nickel*.

1579. The salts of nickel are distinguished by the fine green colour of their solutions, and by affording a green precipitate with ammonia, soluble in excess of that alkali, when it assumes a blue colour. The yellow green precipitate afforded by hydriodate of potassa is very characteristic of nickel; but the nicest test of its presence is the ferro-cyanate of potassa.

Characters
of salts of
nickel.

1580. Of the *Alloys of Nickel* that with iron forms the principal metallic ingredient in those lapideous masses, which, in different countries, have fallen upon our globe, and which have been termed *aërolites*, or *meteoric stones*.†

Alloys.

1581. In meteoric iron the proportion of nickel varies considerably. In a specimen from the arctic region Mr Brande found 3,2 per cent.‡ In that from Siberia Mr Children found nearly 10 per cent.

Meteoric
iron;

The analysis may be performed by solution in nitro-muriatic acid; the iron is thrown down by excess of ammonia in the state of peroxide, of which 100 grains indicate 70 of metallic iron; it is separated by filtration, washed and dried, and on evaporating the filtrated liquor and heating its dry residue red-hot, the oxide of nickel is obtained, which should be redissolved in nitric acid and precipitated by pure potassa, the mixture being boiled for a few seconds. 100 grains of this oxide of nickel are equal to 79 of metallic nickel.§

1582. Meteoric iron has been imitated by fusing iron with nickel. The alloy of 90 iron with 10 nickel is of a whitish yellow cast, and not so malleable as pure iron. The alloy with 3 per cent. of nickel is perfectly malleable and whiter than iron. These alloys are less disposed to rust than pure iron, but nickel alloyed with steel increases the tendency to rust.||

imitated.

1583. The remaining alloys of nickel have been little examined. With copper it forms a hard white alloy, which appears to be the *white copper* of the Chinese.

1584. To detect, in a general way, the presence of nickel in iron, Dr Wollaston recommends that a small quantity (which need not exceed $\frac{1}{1000}$ of a grain) should be filed from the specimen, dissolved in a drop of nitric acid; and evaporated to dryness. A drop or two of pure liquid ammonia, added to the dry mass and gently warmed, dissolves any nickel that may be present. The transparent part of the fluid is then to be led by the end of a glass rod, to a small distance from the precipitated

Dr Wollas-
ton's method
of detecting
nickel in iron.

* *Borate of Nickel* is a pale green insoluble compound.

† For an account of meteoric stones, masses of iron, &c. which have fallen from the heavens, from the earliest period down to 1819, see *Edin. Philos. Jour.* vol. i. p. 221.—See also Cleaveland's *Mineralogy*, p. 773.

‡ *Quarterly Journal*, vi. 369.

§ Children, *Quarterly Journal*, ix. 324.

|| Stodart and Faraday, *Quarterly Journal*.

oxide of iron; and the addition of a drop of triple prussiate of potassa detects the presence of nickel by the appearance of a milky cloud, which is not discernible in the solution of a similar quantity of common wrought iron treated in the same manner. H. 2. 175.

SECTION XXX. Mercury.

1585. Mercury, or quicksilver, is the only one of the metals that retains a fluid form at the ordinary temperature of the atmosphere.

Ore. The principal ore of this metal is the sulphuret, or *native cinnabar*, from which the mercury is separated by distillation with quicklime or iron filings.

Boiling point. 1586. Mercury is a brilliant white metal, having much of the colour of silver, whence the terms *hydrargyrum*, *argentum vivum*, and *quicksilver*. It has been known from very remote ages. According to Crichton it boils and becomes vapour at 656° F., 680° according to Petit and Dulong, 670° Brande. It also rises in vapour in small portions at the common temperature of the atmosphere, particularly in a vacuum.

When the temperature of mercury is considerably increased above its boiling point, the vapour acquires great expansive force, and the power of bursting the strongest vessels. Gay-Lussac has calculated that the vapour of mercury is 12,01 more dense than oxygen gas, and that the liquid metal in becoming gaseous, increases in volume 961 times.

Freezing. 1587. When the temperature of mercury is reduced to about 39° or 40° below zero of Fahrenheit, it becomes solid (147.) and malleable.

By congelation it acquires an increase of specific gravity; and, therefore, unlike other metals, the congealed portion sinks to the bottom of a fluid mass of mercury. Its specific gravity, at 47° above 0 of Fahrenheit, being 13,545, it was found increased by congelation, in an experiment of Mr Biddle, to 15,612, or about one-seventh. H. 2. 123.

Adulteration, how detected. 1588. Mercury is sometimes adulterated with the alloy of lead and bismuth, a fraud easily detected by the want of its due fluidity, and by its not being perfectly volatile, but leaving a residuum when boiled in a platinum or iron spoon.*

* Mercury which is chemically impure will soon acquire adhesive films on its surface, even when cleansed of mechanical impurities, and with a rapidity dependent on the agitation of the metal or extension of surface. These interfere chemically when the metal is to be used in forming combina-

1589. *Mercury and Oxygen*.—Mercury is not oxidized, when pure, at the ordinary temperature of the atmosphere; but preserves the lustre of its surface unchanged for a considerable time. There are several methods, however, by which it may be brought to combine with oxygen. Oxides.

1590. There are two oxides of mercury. The *black*, or *protoxide*, may be obtained by long agitation of the metal in contact with oxygen, or by washing the *proto-chloride of mercury* (calomel) with hot lime-water. It is insipid and insoluble in water, and was called in old pharmacy, *Ethiops per se*.* In this the oxide is mixed, however, with much metallic mercury. Protoxide.

1591. The *red* or *peroxide* of mercury is produced by exposing the metal, heated nearly to its boiling point, to the action of air. It becomes coated with reddish brown scales, spangles, and crystals, and is ultimately entirely converted into a red shining mass, called in old pharmaceutical works, *precipitate per se*, or *calcined mercury*. It is the *hydrargyri oxidum rubrum* of the *London Pharmacopœia*. Peroxide.

It is most easily obtained by introducing into a flat-bottom matrice, fig. 120*, about 4 ounces of mercury, and placing it in a sand-bath, heated to the boiling point of the metal. In about a month's time nearly the whole is converted into oxide. Air is freely admitted by the tube, while its length prevents the escape of mercurial vapour, which condenses and falls back into the body of the vessel; the remaining portion of running mercury may be driven off by exposing it in a basin to a heat just below redness. Pl. vii.
How obtained.

1592. Peroxide of mercury has an acrid metallic taste, and is poisonous; it dissolves very sparingly in water. When heated, it acquires a black colour, but becomes again red on cooling; at a red heat it evolves oxygen, and is reduced to the metallic state. It should be entirely volatilized when placed upon a red-hot iron, for it is sometimes adulterated with red lead. Properties.

Peroxide of mercury, Guibourt finds, is decomposed by long continued exposure to light. It is soluble in water, and communicates to it the property of turning syrup of violets green, and of being precipitated by sulphuretted hydrogen. With ammonia, the peroxide forms an *ammoniuret of mercury*, decomposable by heat. H. 2. 126. Action of light, &c.

tions, and mechanically in its uses in the trough in electro-magnetic experiments, and in the construction of barometers and thermometers.

The purification of mercury from metals by distillation should be performed in an iron retort, a portion of clean iron and copper filings having been introduced with the mercury, which should be condensed and received in clean water. This process, however, is not wholly unobjectionable, as both zinc and arsenic will pass over, and these metals are often present. A very useful method is to put from half an inch to an inch in depth of mercury, into a large earthenware pan, and to pour over it sulphuric acid diluted with twice its weight of water. The substances should be left together for a week or two, being frequently agitated. The metal and acid are then to be separated, the latter preserved for a similar operation in future, and the former washed, dried and cleansed mechanically, by squeezing through shamois leather, by agitation with damp loaf sugar, passing through a paper funnel, &c.—See Faraday's *Chem. Manip.* sect. xx.

* It is the *Hydrargyri Oxidum cinereum* of the U. S. Pharmacopœia.

1593. It appears from the researches of Donovan* and Sefstrom,† which are confirmed by Dr Thomson, that these oxides are thus constituted:

| | Metal. | Oxygen. |
|-------------------|-------------|----------|
| Protoxide | 200 | 8 = 208 |
| Peroxide | 200 | 16 = 216 |

1594. Mercury unites easily with chlorine, and if heated in that gas, burns with a pale red flame. The product is identical with the salt, called *corrosive sublimate*, which in fact is a chloride of mercury, and is termed *per-chloride* or *bi-chloride* to distinguish it from *calomel*,‡ another compound of the same elements in different proportions.

1595. *Proto-chloride of Mercury*.—This compound, commonly termed *calomel*, is first mentioned by Crolius, early in the seventeenth century. The first directions for its preparation are given by Beguin, in the *Tyrocinium Chemicum*, published in 1608. He calls it *draco mitigatus*.§

The most useful mode of preparing calomel consists in triturating two parts of corrosive sublimate with one of mercury, until the globules disappear, and the whole assumes the appearance of an homogeneous grey powder, which is introduced into a matrice, placed in a sand heat, and gradually raised to redness. The calomel sublimes, mixed with a little corrosive sublimate, the greater part of which, however, being more volatile than the calomel, rises higher in the matrice; that which adheres to the calomel may be separated, by reducing the whole to a fine powder, and washing in large quantities of hot distilled water. Pure calomel, in the form of a yellowish white insipid powder, remains.||

1596. It will be observed, that in the processes the operation consists in reducing the perchloride to the state of protochloride by the addition of mercury. Various modes have, however, been adopted for the direct formation of calomel: two of these may here be noticed, of which the first is in the humid way, as devised by Scheele and Chenevix. They are given below.¶

* *Ann. of Philos.* xiv.

† *Ibid.* iii. 355.

‡ In the *U. S. Pharmacopœia* they are termed *submuriate of mercury* and *oxymuriate of mercury*.

§ Several other fanciful names have been applied to it, such as *aquila mitigata*, *manna metallorum*, *panchymagogum minerale*, *sublimatum dulce*, *mercurius dulcis*, &c.

|| It was formerly the custom to submit calomel to very numerous sublimations, under the idea of rendering it *mild*; but these often tended to the production of corrosive sublimate; and the calomel of the first sublimation, especially if a little excess of mercury be found in it, is often more pure than that afforded by subsequent operations.

The following are the directions given in the last *London Pharmacopœia*:

“Take of oxymuriate of mercury, 1 lb.

purified mercury, *by weight*, 9 oz.

Rub them together, until the metallic globules disappear; then sublime: take out the sublimed mass, reduce it to powder, and sublime it in the same manner twice more successively. Lastly, bring it to the state of a very fine powder; throw this into a large vessel, full of water; then stir it, and, after a short interval pour the supernatant turbid solution into another vessel, and set it by, that the powder may subside. Lastly, having poured away the water, dry the powder.”

Powell's *Translation of the London Pharmacopœia*, London, 1815, p. 144 and 99. See also *U. S. Pharmacopœia*, 141.

¶ Form a nitrate of mercury, by dissolving as much mercury as possible in hot nitric acid; then dissolve in boiling water a quantity of common salt, equal to half the weight of the mercury used, and render the solution sensibly sour by muriatic acid, and pour the hot nitrate of mercury into it. Wash and dry the precipitate.

If this process be carefully performed, and the precipitate thoroughlyedulcorated, the calomel is sufficiently pure.

The second process, however, or that by which calomel is directly formed in the dry way, appears,

1597. Proto-chloride of mercury is usually seen in the form of a white mass, of a crystalline texture, and when very slowly sublimed, it often presents regular four-sided prisms, perfectly transparent and colourless. Its specific gravity is 7.2. It is tasteless, and very nearly insoluble in water. It can scarcely be called poisonous, since in considerable doses it only proves purgative. By exposure to light it becomes brown upon its surface. If scratched, it gives a yellow streak, which is very characteristic, and does not belong to the perchloride. When very finely levigated it becomes of a buff colour.

Characters.

It consists of 1 proportional of mercury 200 + 1 proportional of chlorine 36, and its representative number is 236.

Composition.

| | | | | | | |
|-------------|-----------|----|-----------|-------|--------|-------|
| Or, Mercury | | 85 | | 100 | 1 atom | 200 |
| Chlorine | | 15 | | 17,6 | 1 " | 36 |
| | | | | <hr/> | | <hr/> |
| | | | | 100. | | 236.* |

1598. It is decomposed when boiled with a solution of muriate of soda, and still more readily and completely by muriate of ammonia, which converts it entirely into bi-chloride and mercury, the former remaining in solution.† If therefore either of these salts be employed, as is recommended, to dissolve any corrosive sublimate remaining in calomel, they should be used only in cold and very dilute solutions. H.

Decomposed by muriate of ammonia.

1599. *Perchloride of Mercury*—*Bichloride*, or *corrosive sublimate*, may be obtained by a variety of processes.

Perchloride, or Corrosive sublimate.

When mercury is heated in chlorine, it burns with a pale flame; the gas is absorbed, and a white volatile substance rises, which is the perchloride.

It may also be obtained by dissolving peroxide of mercury in muriatic acid, evaporating to dryness, re-dissolving in water, and crystallizing.

1600. The ordinary process for making corrosive sublimate consists in exposing a mixture of chloride of sodium (common salt) and bi-sulphate of the peroxide of mercury, to heat in a flask, or other proper subliming vessel; a mutual decomposition ensues. The chlorine of the common salt unites to the mercury of the sulphate, and forms bi-chloride of mercury. The oxygen of the oxide of mercury converts the sodium of the salt into soda, which, with the sulphuric acid, produces sulphate of

Theory of the process.

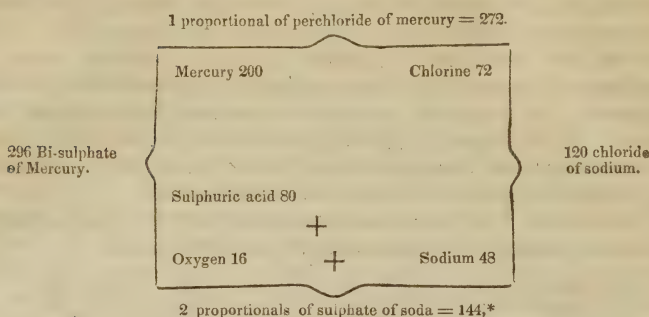
on the whole, the least exceptionable for the production of this very important article of pharmacy; it is the method followed at Apothecaries' Hall, sanction having been obtained for its adoption from the College of Physicians.

50 lbs of mercury are boiled with 70 lbs of sulphuric acid, to dryness, in a cast-iron vessel: 62 lbs of the dry salt are triturated with 40 1-2 lbs of mercury, until the globules disappear, and 34 lbs of common salt are then added. This mixture is submitted to heat in earthen vessels, and from 95, to 100 lbs of calomel are the result. It is to be washed in large quantities of distilled water, after having been ground to a fine and impalpable powder.

* *Native Chloride of Mercury* or *mercurial horn ore*, has been found in Germany, France, and Spain, usually crystallized, and sometimes incrusting and massive.

† *Quar. Jour.* xviii. 295.

soda. This decomposition is exhibited by the following diagram :



Composition.

1601. By the quantity of chlorine absorbed by a given weight of mercury, we learn that the perchloride of mercury consists of 1 proportional of mercury = 200 + 2 proportionals of chlorine = 72, consequently its representative number is 272.

Characters.

1602. Perchloride of mercury is usually seen in the form of a perfectly white semi-transparent mass, exhibiting the appearance of imperfect crystallization. It is sometimes procured in quadrangular prisms. Its taste is acrid and nauseous, leaving a peculiar metallic and astringent flavour upon the tongue. It dissolves in 20 parts of water at 60°, and in about half its weight at 212°. It is more soluble in alcohol than in water. When heated, it readily sublimes in the form of a dense white vapour, strongly affecting the nose and mouth. It dissolves without decomposition in muriatic, nitric, and sulphuric acids: the alkalies and several of the metals decompose it. It produces, with muriate of ammonia, a very soluble compound; hence a solution of sal-ammoniac is used with advantage in washing calomel to free it from corrosive sublimate.

1603. Protochloride and perchloride of mercury are decomposed by potassa, soda and lime; the former affords *black* (*hydrargyri oxidum cinereum* of the *London*, and *U. S.*

* The following are the official directions of the *London* (and *U. S.*) *Pharmacopæia*, for the preparation of corrosive sublimate, there termed *oxymuriate of mercury*.

— Take of purified mercury, *by weight*, 2 lbs.

— sulphuric acid, *by weight*, 30 oz.

— dried muriate of soda, 4 lbs.

Boil the mercury with the sulphuric acid in a glass vessel, until the sulphate of mercury is left dry. Rub this when it is cold with the muriate of soda in an earthen-ware mortar; then sublime it in a glass cu-curbit, increasing the heat gradually."—Powell's *Translation*.

The quantity of common salt employed in this process is obviously too large; in practice, however, we find that more than the real quantity decomposed, and shown in the above table, is required.

The following is the process employed at Apothecaries' Hall for the formation of corrosive sublimate: 50 lbs of mercury are boiled to dryness with 70 lbs of sulphuric acid. 73 lbs of persulphate of mercury are thus formed, which being perfectly mixed with 120 lbs of common salt and sublimed, yield from 63 to 65 lbs of corrosive sublimate. B.

Pharmacopœia;) the latter *red*, oxide of mercury; and the chlorides of potassium, sodium, and calcium, are produced.*

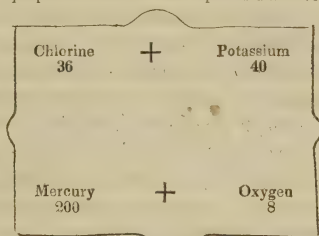
1604. When solution of ammonia is poured upon calomel, protoxide of mercury, and muriate of ammonia, are the results; but ammonia, added to a solution of corrosive sublimate, occasions a white precipitate of a *triple muriate of ammonia and mercury*.†

1605. The presence of mercury in a fluid supposed to contain corrosive sublimate may be detected by concentrating and digesting it with an excess of pure potassa. The oxide of mercury, which subsides, is then sublimed in a small glass tube by means of a spirit lamp, and obtained in the form of metallic globules.‡ A very elegant method of detecting the presence of mercury is to place a drop of the suspected liquid on polished

* The following diagrams show the interchange of elements that takes place in the case of adding a solution of potassa to protochloride and perchloride of mercury.

1 proportional of chloride of potassium = 76.

1 proportional of
protochloride of
mercury = 236.

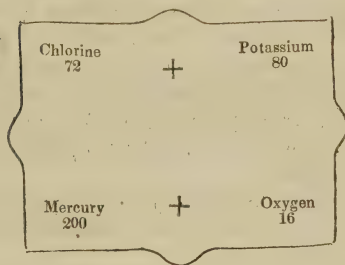


1 proportional of
potassa = 48.

1 proportional of protoxide of mercury = 208.

2 proportionals of chloride of potassium = 152.

1 proportional of
perchloride of
mercury = 372.



2 proportionals of
potassa = 96.

† A compound of this kind has long been used in pharmacy, under the name of *calx hydrargyri alba* or *white precipitate*. The London and U. S. Pharmacopœia direct the following process for its formation.

- Take of oxymuriate mercury 1-2 lb.
- muriate of ammonia 4 oz.
- solution of subcarbonate of potassa 1-2 pint.
- distilled water 4 pints.

First dissolve the muriate of ammonia, then the oxymuriate of mercury, in the distilled water, and add thereto the solution of subcarbonate of potassa. Wash the precipitated powder until it becomes tasteless: then dry it.

In the U. S. Phar. it is termed *Hydrargyri Submuriatis Ammoniacus*.

‡ According to Dr Christison, this and other processes recommended by medical jurists for the detection of corrosive sublimate in mixed fluids, are not altogether satisfactory.

gold, and to touch the moistened surface with a piece of iron wire on the point of a penknife, when the part touched instantly becomes white, owing to the formation of an amalgam of gold. T. 435.*

Chlorate.

1606. *Chlorate of Mercury*.—Chloric acid dissolves both the oxides of mercury; the *protochlorate* has the appearance of a yellowish, granular powder, sparingly soluble in hot water, and of a mercurial taste. The *perchlorate* forms white acicular crystals, having the acid flavour of the perchloride.†

1607. *Mercury and Bromine*.—By the action of bromine on metallic mercury, a compound results which yields the peroxide of mercury when decomposed by alkalies, and is a bi-bromuret. It may be sublimed by heat, is soluble in water, alcohol, and ether, particularly in the last, and presents a close analogy to corrosive sublimate. It is distinguished from that substance, however, by yielding the red vapours of bromine when treated by the nitric, and still better by the sulphuric acid. T.

Iodide.

1608. *Mercury and Iodine* unite in two proportions. These compounds may be procured either by gently heating mercury with iodine, or by adding hydriodic acid to solutions of mercury. The *protiodide* is yellow, and the *periodide* red. They respectively consist of 1 proportional of mercury + 1 of iodine and 1 + 2. They are both insoluble in water.‡

Nitrates.

1609. *Mercury and Nitric Acid*.—Nitric acid is rapidly decomposed by mercury; nitrous acid, and nitric oxide gases are evolved, and either a protonitrate or a pernitrate of mercury is obtained, according to the mode in which the solution is performed.

1610. *Protonitrate of Mercury* is best obtained by dissolving the metal in a cold and dilute acid, consisting of one part of acid and three of water; the metal should be added in small successive portions until the acid ceases to act upon it, and care should be taken to keep the whole cold. This solution deposits transparent crystals which consist of 1 atom of acid, 1 of protoxide, and 2 of water.

This salt dissolves completely in water slightly acidulated with nitric acid, but in pure water a small quantity of a yellow sub salt is generated.

1611. *Pernitrate of Mercury*.—When mercury is dissolved in hot and concentrated nitric acid, it becomes peroxidized, and furnishes prismatic crystals of the pernitrate, composed of 1 atom acid and 1 atom of peroxide. Their solution furnishes yellow or red precipitates of the peroxide of mercury, upon the addition of potassa or soda, and ammonia forms a white precipitate which is a *triple nitrate of mercury and ammonia*.

* This process was originally suggested by Mr Silvester, and has since been simplified by Dr Paris's *Medical Jurisprudence*, by Paris and Fonblanque.

† Vauquelin, *Annales de Chimie*, xci.

‡ *Iodate of Mercury*.—Iodate of potassa occasions a precipitate in protonitrate of mercury, but not in the pernitrate.

When the precautions in forming the nitrates above described are not attended to, the solution usually contains a mixture of the two nitrates, and furnishes a precipitate with the alkalis, composed of both oxides. The pernitrate is most certainly formed by dissolving the red oxide in nitric acid.*

1612. When hot water is poured upon pernitrate of mercury, a yellow insoluble powder separates from it, which is a *subpernitrate*, the *nitrous turpeth* of old writers; and a *super-pernitrate* remains in solution. It seems probable that the protonitrate is also capable of affording a sub and super nitrate, but all these compounds have hitherto been but imperfectly investigated, and new researches are wanting to establish their nature and composition.

1613. When these nitrates of mercury are exposed to heat gradually raised to dull redness, nitric acid is given off; and a brilliant red substance remains, consisting of peroxide of mercury with a small portion of adhering nitrate. This is used in pharmacy as an *escharotic*, and is called in the U. S. Pharmacopœia *hydrargyri nitrico-oxidum*.†

1614. *Fulminating Mercury*.—Mercury is the basis of a *fulminating compound* discovered by the late Mr E. Howard.

To prepare this powder, 100 grains (or a greater proportional quantity, not exceeding 500,) are to be dissolved with heat, in a measured ounce and a half of nitric acid. The solution being poured cold upon two measured ounces of alcohol, previously introduced into a convenient glass vessel, a moderate heat is to be applied till effervescence is excited. A white fume then begins to undulate on the surface of the liquor, and the powder will be gradually precipitated on the cessation of action and reaction. The precipitate is to be immediately collected on a filter, well washed with distilled water, and cautiously dried in a heat not exceeding that of a water-bath. The immediate washing of the powder is material, because it is liable to the reaction of the nitric acid; and while any of that acid adheres to it, it is very subject to be decomposed by the action of light. From 100 grains of mercury, about 120 or 130 of the powder are obtained.‡

This powder has the property of detonating loudly in a gentle heat, or by light friction. Hence it has been proposed as a means of firing ordnance. But an accident described by Professor Silliman, as having happened in his laboratory, shows that this fulminating compound explodes from such trifling causes, as not to be kept without danger, even when secured from fric-

* According to M. Souberain, if ammonia be added gradually to a very weak solution of pure protonitrate of mercury, two precipitates are obtained, one of a grey black, and the other white; the latter being most abundant the nearer the precipitation is to its termination. If the precipitate be thrown down and removed in separate portions, the white preparation may be obtained nearly pure; it is insipid, inodorous, and insoluble in water. It is not attacked by caustic alkalies, or by nitric or sulphuric acid. Its composition is, 4 atoms of protoxide, 1 of nitric acid, and 1 of ammonia.

The ammoniaco-deuto-nitrate may be obtained by adding excess of ammonia to a dilute solution of the deuto-nitrate of mercury. The white precipitate obtained is insoluble in water, but soluble in muriatic acid, from which potassa or soda precipitates it: ammonia produces a precipitate in the solution, resolvable in excess of the alkali: nitric and sulphuric acids partly dissolve it. It contains 2 atoms of deutoxide of mercury, 1 of ammonia, and 1 of nitric acid. *Bull. Univ. A. vii. 210.*

† In the manufacture of this compound at Apothecaries' Hall, (Lond.) 100 lbs. of mercury are boiled with 48 lbs of nitric acid (sp. gr. 1.48) and by proper evaporation and application of a dull red heat, 112 lbs of the *hydrargyri nitrico oxidum* are obtained. B.

‡ See *Phil. Trans.* 1800, p. 214.

tion and heat.* H. 2. 130. It is a compound of mercury and cyanic acid. 799.†

Sulphuret.

1615. *Mercury and Sulphur*.—When one part of mercury is triturated for some time with three of sulphur, a black, tasteless compound is obtained, which Mr Brande has shown to be a mixture of sulphur and the bi-sulphuret of mercury.‡ It was called in old pharmacy *Ethiops Mineral*; it is the *hydrargyri sulphuretum nigrum* of the U. S. Pharmacopœia.§

The same substance is more readily formed by pouring mercury into melted sulphur, the substances quickly combine, with such a rise of temperature as often produces inflammation.

1616. There is some difficulty in ascertaining how far these are definite compounds; when, however, sulphuretted hydrogen is passed through a dilute solution of nitrate of mercury, a black powder is thrown down, which appears to be a true sulphuret, and which, according to Guibourt,|| consists of 100 mercury + 8,2 sulphur, numbers which nearly correspond to

$$\begin{array}{rcl} 1 \text{ proportional mercury} & = & 200 \\ 1 \text{ ————— sulphur} & = & 16 \\ \hline \text{Sulphuret of mercury} & = & 216 \end{array}$$

1617. When the black sulphuret is heated red-hot in a flask, a portion of mercury evaporates, and a sublimate of a steel grey colour is obtained, which, when reduced to a fine powder, assumes a brilliant red colour, and is called *vermillion* or *cinnabar*. It is, in fact, a *bi-sulphuret of mercury*, and consists of

$$\begin{array}{rcl} 1 \text{ proportional of mercury} & = & 200 \\ 2 \text{ ————— sulphur} & = & 32 \\ \hline \text{Bi-sulphuret of mercury} & = & 232 \end{array}$$

Manufacture
of cinnabar.

1618. In the manufacture of cinnabar 8 parts of mercury are mixed in an iron pot with one of sulphur, and made to combine by a moderate heat, and constant stirring: this compound is then transferred to a glass subliming vessel, (on a small scale a Florence flask answers perfectly,) and heated to redness in a sand-bath; a quantity of mercury and of sulphur evaporate, and a sublimate forms which is removed, and rubbed or levigated into a very fine powder.

1619. Cinnabar is not altered by exposure to air or moisture; when heated to dull redness in an open vessel, the sulphur forms sulphurous acid, and the mercury escapes in vapour. It is decomposed by distillation with fixed alkalies, lime, and baryta, and by several of the metals. When adulterated with red lead it is not entirely volatile.

1620. Cinnabar may be made in the humid way by long trituration of mercury and sulphur in solution of potassa.¶

* *Amer. Jour* i. 168.

† See *Fulminating Silver*.

‡ *Quart. Jour.* xviii. 294.

§ It is no longer retained in the *London Pharmacopœia*.

|| *Ann. de Chimie et Phys.* Tom. ii.

¶ *Nicholson's Journal*, iv. to ii.

1621. *Native Cinnabar* is the principal ore of mercury: it occurs massive and crystallized of various colours, sometimes appearing steel grey, at others bright red. Native mercury, and native amalgam of silver sometimes accompany it.* Native cinnabar.

1622. *Mercury and Sulphuric Acid*.—When mercury is boiled in its weight of sulphuric acid, sulphurous acid gas is evolved, a part of the metal is oxidized and dissolved and a white deliquescent mass is obtained, which, washed with cold water, affords a very difficultly soluble white salt, which is a *proto-sulphate of mercury*. It requires 500 parts of water for its solution. It consists of Sulphates:

12 sulphuric acid
83 protoxide of mercury
5 water.

According to theory, it should consist of one proportional of sulphuric acid + 1 of protoxide, or

40 sulphuric acid
208 protoxide of mercury

248 sulphate of mercury.

The alkalis precipitate black oxide of mercury from this salt.

1623. If three parts of sulphuric acid be boiled to dryness, with one of mercury, a white mass of *persulphate of mercury* is obtained; it is more soluble than the sulphate and crystallizes in prisms. According to Braamecamp and Oliva, it is composed of 31,8 acid, 63,8 peroxide, 4,4 water. Persulphates.

It should consist, according to theory, of one proportional of peroxide + 2 proportionals of acid.

1624. When hot water is poured upon persulphate of mercury, a yellow, insoluble *subpersulphate* is formed, formerly called *Turpeth mineral*.† It appears to consist of 1 proportional of peroxide + 1 of acid.

The principal use of sulphate of mercury is in the formation of corrosive sublimate and calomel.

1625. The solutions of persulphate of mercury furnish red precipitates with the fixed alkalis, and white with ammonia, the latter being a triple *sulphate of ammonia and mercury*.

1626. Sulphuretted hydrogen produces a black precipitate in solutions of mercury when added in excess, and which appears to be a sulphuret of mercury.‡

1627. *Mercury and Cyanogen*.—Cyanide of mercury may be prepared by boiling in a matrice eight parts of water, two of finely powdered prussian blue, and one of peroxide of mercury.

* *Hyposulphite of Mercury* appears not to exist: when a solution of a hyposulphite is poured into a very dilute solution of protonitrate of mercury it occasions a black precipitate.

† *Hydrargyri subsulphas flavus* of the U. S. Pharmacopœia.

‡ *Phosphuret of Mercury* may be formed by heating phosphorus with oxide of mercury. It is a sectile solid of a bluish black colour.

When phosphate of soda is added either to nitrate or pernitrate of mercury, a white precipitate is formed. There is probably a *protophosphate* and a *perphosphate*. The latter is soluble in excess of acid.

Mercury and Carbonic Acid.—Alkaline carbonates produce buff-coloured precipitates in solutions of both oxides of mercury. These are probably the *protocarbonate* and the *percarbonate*.

When the liquid assumes a yellow colour, it is to be filtered, and the cyanide of mercury is deposited in a crystallized form on cooling.* By repeated evaporation and cooling, all the cyanide that is capable of crystallizing will be separated, mingled, however, with some oxide of iron. To purify it, Proust recommends that it be re-dissolved; boiled with an excess of oxide of mercury; and again filtered. The liquid retains an excess of the oxide, which may be saturated by adding hydrocyanic acid, for the oxygen instantly passes to the hydrogen of the acid, and the cyanogen to the mercury. The cyanide may now be crystallized again; and, if intended for the preparation of cyanogen, it must be thoroughly dried, avoiding, however, more heat than is absolutely necessary. H. 2. 129.†

1628. The cyanide of mercury, when pure, is colourless and inodorous, has a very disagreeable metallic taste, and is highly poisonous. It does not affect the colour of litmus or turmeric paper. When strongly heated it is converted into cyanogen and metallic mercury. (777.) It is more soluble in hot than in cold water, and is dissolved in that liquid without change. The solution has not the characteristic odour of the salts of hydrocyanic acid, nor do alkalies throw down the oxide of mercury.

It is composed of 200 parts, or 1 atom of mercury, and 52 parts or 2 atoms of cyanogen. T. 437.‡

1629. *Chromate of Mercury*.—Chromate of potassa throws down an orange-coloured precipitate from the solutions of nitrate and pernitrate of mercury.

1630. The soluble salts of mercury furnish whitish precipitates with ferro-cyanate of potassa, and black with sulphuretted hydrogen. A plate of copper, immersed into their solutions, occasions the separation of metallic mercury.

The insoluble mercurial salts are mostly entirely volatilized at a red heat; if distilled with charcoal, they afford metallic mercury.

1631. Mercury combines with most of the other metals, and forms a class of compounds which have been called *amalgams*.

* Described *Ann. of Philos.* N. S. vi. 42. According to Gay-Lussac, the crystals are composed of 80 mercury + 20 cyanogen. They probably contain 1 proportional of mercury and 2 of cyanogen. B.

† Dr Turner recommends that the prussian blue should be previously purified by digestion in diluted muriatic acid, being then washed and dried, 8 parts of the purified substance, with 11 of the peroxide of mercury, should be boiled together in water; the former substance is entirely decomposed, and a colourless solution obtained, which on evaporation yields pure white crystals of cyanide of mercury, even to the last drop. He also recommends the preparation of the pure ferro-cyanate of iron from the ferro cyanate of potassa and a per-salt of iron, as being far more economical than the prussian blue of commerce. Brewster's *Journal*, v. 245.

‡ *Borate of Mercury*, obtained by adding borate of soda to nitrate of mercury, is a yellow insoluble powder.

Arseniates of Mercury.—Arsenic acid occasions a pale yellow precipitate in solution of protonate of mercury, and a yellowish white precipitate in solution of the pernitrate. Arsenious acid produces white precipitates in both solutions.

Molybdic acid occasions a white precipitate in solution of nitrate of mercury.

These are generally brittle or soft. One part of potassium with 70 of mercury produce a hard brittle compound. If mercury be added to the liquid alloy of potassium and sodium, an instant solidification ensues, and heat enough to inflame the latter metal is evolved. The use of an amalgam of zinc and mercury has already been adverted to for the excitation of electrical machines. The amalgams of gold and silver are employed in gilding and silvering.

An amalgam of 2 parts of mercury, 1 of bismuth, and 1 of lead, is fluid, and when kept for some time, deposits cubic crystals of bismuth.

Amalgam of copper may be made as follows :

To a hot solution of sulphate of copper, add a little muriatic acid, and a few sticks of zinc, and boil the mixture for about a minute : by this means the copper will be precipitated in a metallic state, and in a finely divided spongy form : take out the zinc, pour off the liquor, wash the copper with hot water, and pour upon it a little dilute nitrate of mercury, which will instantly cover every particle of copper with a coating of mercury : then add mercury to the amount of two or three times the weight of the copper, and a slight trituration will combine them so far that the completion of the process may be effected by heating the mixture for a few minutes in a crucible.*

Amalgam of copper.

1632. By combination with mercury, metals that are not easily oxidized, acquire a facility of entering into union with oxygen. Thus gold and silver, when combined with mercury, are oxidized by ignition in contact with air. This fact furnishes a striking illustration of the effect of overcoming the aggregative affinity of bodies in promoting chemical union. H.

Oxidation of metals promoted by mercury.

1633. When mercury is negatively electrized in a solution of ammonia, or when an amalgam of potassium and mercury is placed upon moistened muriate of ammonia, the metal increases in volume, and becomes of the consistency of butter, an appearance which has sometimes been called the *metallization of ammonia*. The compound appears only to contain ammonia and mercury, though its real nature has not been satisfactorily ascertained. It has suggested some hypotheses concerning the nature of ammonia and the metals, which are not worth recording.

SECTION XXXI. Osmium.

1634. Osmium, and the metals described in the three following sections are contained in the ore of platinum.

This ore is digested in nitro-muriatic acid, by which the greater portion is dissolved, and there remains a black powder, which, when fused with potassa and washed, furnishes a yellow alkaline solution of oxide of osmium. Saturate the alkali with sulphuric acid, pour the mixture into a retort, and distil. A colourless solution of the *oxide of osmium* passes into the receiver ; it has a sweetish taste and a very peculiar smell, somewhat like that of new bread.† When mercury is shaken with this solution it becomes an amalgam, which is decomposed by distillation and pure osmium remains.

Process for obtaining osmium

* Aikin's Dictionary, Art. Mercury, p. 92.

† Hence the name from *οσμῆν*, odour.

1635. Osmium has a dark grey colour, and is not volatile when heated in close vessels; but heated in the air it absorbs oxygen, and forms a volatile oxide. It has not been fused.

Characters.

1636. The leading characters of osmium are its insolubility in the acids, its ready solubility in potassa, the facility with which it is oxidized, the singular smell of its oxide, its great volatility, and the purple or blue colour produced in its solution by tincture of galls. The other compounds have scarcely been examined.

1637. M^r Laugier having observed that nitro-muriatic acid, which has been employed to dissolve platinum, emits a strong odour of osmium, distilled the liquor and saturated the product with quick-lime; after which by again distilling the liquid, he obtained a quantity of osmium sufficient to repay the trouble of the process.* H.

SECTION XXXII. Iridium.

How obtained.

1638. The black powder mentioned in the last section contains iridium, which resists the action of potassa, and consequently remains after the separation of osmium. A solution of its oxide may be procured by digesting it in muriatic acid, which first becomes blue, then olive-green, and lastly, red. By alternate treatment with potassa and muriatic acid, the whole of the black powder will be dissolved. By evaporating the muriatic solution to dryness, dissolving the dry mass in water, and evaporating a second time, octoëdral crystals of muriate of iridium are obtained.

Method of obtaining from the muriate.

1639. Iridium is obtained by immersing a plate of zinc into a solution of the muriate, or by violently heating the octoëdral crystals. It is of a whitish colour, and according to Mr Children, who succeeded in fusing it by means of his large voltaic apparatus, its specific gravity is above 18. Its most marked character is extremely difficult solubility in the acids.

1640. In crude platinum Dr Wollaston discovered some flat white grains which resisted the action of the acids, and which he ascertained to consist of a *native alloy of osmium and iridium*.

Discovery.

1641. Osmium and iridium were discovered by Mr Tennant in 1803. The name of the latter is derived from the variety of colours exhibited by its solution.†

* *Ann. de Chim.* 91. p.191.

† *Phil. Trans.* 1804.

SECTION XXXIII. *Rhodium.*

1642. Rhodium and Palladium were discovered by Dr Wollaston in 1803.* These, like the two last described metals, exist in the ore of platinum, from which rhodium may be obtained by the following process : Discovery.

Digest crude platinum in a small quantity of nitro-muriatic acid, filter the saturated solution, and pour it into a solution of sal ammoniac, by which the greater proportion of the platinum is precipitated. Decant the clear liquor and immerse a plate of zinc, which becomes coated with a black powder. Separate this and digest it in dilute nitric acid, by which a little copper and lead are taken up. Then wash and digest in dilute nitro-muriatic acid, to which add some common salt, evaporate to dryness, and wash the dry mass repeatedly with alcohol. A deep red substance remains, which, when dissolved in water, furnishes a black precipitate upon the immersion of a plate of zinc. This strongly heated with borax, assumes a white metallic lustre, and is rhodium. How obtained.

1643. Rhodium is very difficult of fusion ; its specific gravity is 10,6. When an alloy of lead and rhodium is digested in nitro-muriatic acid, it is dissolved, and by evaporation a red compound is obtained, from which muriate of rhodium may be separated by water, or more perfectly by alcohol. The rose-colour of this compound suggested the name which has been applied to the metal. Properties.

1644. Berzelius has described three oxides of this metal, composed as follows : Oxides.

| | Metal. | Oxygen. |
|-------------------|--------|---------|
| Protoxide | 100 + | 6,71 |
| Dentoxide | 100 + | 13,42 |
| Peroxide | 100 + | 20,13 |

Dr Thomson considers the existence of two oxides of rhodium as established, the black or protoxide, and the yellow, which, according to him, are constituted as follows :

| | Metal. | Oxygen. | Metal. | Oxygen. |
|-------------------|--------|--------------|--------|---------|
| Protoxide | 100 + | 18,2 or 44 + | 8 | |
| Peroxide | 100 + | 36,4 or 44 + | 16 | |

1645. Rhodium forms malleable alloys with the malleable metals, several of which have been examined by Dr Wollaston.† Alloys.

With steel rhodium forms an alloy, which probably would be very useful in the arts, were it not for the scarcity of the latter metal. 1 to 2 per cent. of rhodium gives steel great hardness, and yet there is sufficient tenacity to prevent cracking either in forging or hammering.‡

SECTION XXXIV. *Palladium.*

1646. Palladium is most easily obtained by the following process.§ Digest the ore of platinum in nitro-muriatic acid, How obtained.

* Palladium was also discovered by Mr Cloud, in a native alloy of gold with that metal.

† *Phil. Trans.* 1804. Thomson's *System*, vols. i. and ii.

‡ *Quart. Jour.* ix. 328.

§ Wollaston, *Phil. Trans.* 1805.

neutralize the redundant acid by soda, throw down the platinum by muriate of ammonia, and filter. To the filtered liquor add a solution of cyanide of mercury: a yellow flocculent precipitate is soon deposited, which yields palladium on exposure to heat.*

Properties.

1647. Palladium is of a dull white colour, malleable and ductile. Its specific gravity is about 11. It is hard. It fuses at a temperature above that required for the fusion of gold.

1648. Dr Wollaston has ascertained the existence of *native palladium* in the ore of platinum. It is in small fibrous grains.

Action of acids and alkalies.

1649. Muriatic acid boiled upon palladium acquires a fine red colour. Sulphuric acid becomes blue. Nitric acid readily dissolves it; but its best solvent is the nitro-muriatic, which forms a fine red solution. The alkalies throw down an orange-coloured precipitate from these solutions, sparingly soluble in the alkalies. Ferro-cyanate of potassa gives an olive-green precipitate; and sulphuretted hydrogen, one of a dark brown colour.

Oxides.

1650. Berzelius has shown that 100 parts of palladium unite with 14,209 parts of oxygen. Hence the oxide consists of

| | |
|---------------------|-------|
| Palladium | 87,56 |
| Oxygen | 12,44 |

100.

Sulphuret.

1251. Palladium readily combines with sulphur. The compound is whiter than the separate metal, and is very brittle. It has been investigated by Berzelius, and shown to be composed as follows:

| | | | |
|---------------------|-------|-----------|--------|
| Palladium | 78,03 | | 100, |
| Sulphur | 21,97 | | 28,15 |
| | | | <hr/> |
| | 100 | | 128,15 |

Equivalent number.

1652. The equivalent number for the metal, deducible both from the oxide and sulphuret is 56,2. We may, therefore, denote the weight of its atom by 56, that of the oxide by 64; and of the sulphuret by 72. H. 2. 164.

SECTION XXXV. *Silver.*

Native silver.

1653. Silver is found native, and in a variety of combinations.

Native silver has the general characters of the pure metal. It occurs in masses; arborescent; capillary; and, sometimes, crystallized in cubes and octoëdra. It is seldom pure, but con-

*See also a process by Vauquelin, in *Ann. Philos.* vols. iv. and vii.

tains small portions of other metals, which affect its colour and ductility. It is chiefly found in primitive countries. In Peru and Mexico are the richest known mines of native silver.

1654. To obtain silver in a state of purity, Mr Donovan recommends, that 240 grains of standard silver be dissolved in as much pure nitric acid of specific gravity about 1.2, as will be barely necessary for solution. This is to be filtered, and distilled water allowed to run through the filter, until the fluids amount to two ounce measures. A bright plate of copper weighing upwards of 64 grains, is to be immersed and frequently agitated in it. When the silver has entirely precipitated, which will very soon happen, the clear supernatant liquor is to be poured off, and the precipitate to be well washed with pure water. The silver is then to be boiled for a few minutes in liquid ammonia. It is then to be well washed with water and dried on a filter, after which, if required, it may be melted in a crucible.*†

Methods of
obtaining
pure silver

It may also be procured by adding to the above solution of standard silver a solution of common salt; collect, wash, and dry the precipitate, and fuse it with its weight of carbonate of potassa. A button of the pure metal is thus obtained.

1655. Silver has a pure white colour, and considerable brilliancy. Its specific gravity is 10.5. It is so malleable and ductile, that it may be extended into leaves not exceeding a ten-thousandth of an inch in thickness, and drawn into a wire finer than a human hair.

Characters.

1656. Silver melts at a bright red heat, and when in fusion appears extremely brilliant. It resists the action of air at high temperatures for a long time, and does not oxidize; the *tarnish* of silver is occasioned by sulphurous vapours; it takes place very slowly upon the pure metal, but more rapidly upon the alloy with copper used for plate, and was found by Proust to consist of sulphuret of silver. Pure water has no effect upon the metal; but if the water contain vegetable or animal matter, it often slightly blackens its surface in consequence of the presence of sulphur. If an electric explosion be passed through fine silver wire, it burns into a black powder, which is an oxide of silver. In the voltaic circle it burns with a fine green light, and throws off abundant fumes of oxide. Exposed to an intense white heat, it boils and evaporates. If suddenly cooled, it crystallizes during congelation, often shooting out like a cauliflower, and throwing small particles of the metal out of the crucible.

Tarnish.

Effect of
water.

— of heat.

1657. Silver is not unfrequently obtained in considerable quantities from argentiferous sulphuret of lead, which is reduced in the usual way and then *cupelled*; the oxide of lead thus procured is afterwards reduced by charcoal.

Some of the silver ores, especially the sulphurets, are reduced by amalgamation. These ores, when washed and ground, are mixed with a portion of common salt and roasted; they are then

* *Phil. Mag.* xlvii. 205.

† Dr Thomson found it difficult to obtain silver free from copper, even when reduced from the chloride, but accomplished the object by first washing the chloride with diluted nitric acid, which removed the copper. *First Principles*, ii. 436.

powdered and mixed by agitation with mercury, and the amalgam thus formed is distilled.*

1658. From some curious facts which are stated by Mr Lucas,† it appears that silver, when melted, and exposed to a current of air or of oxygen gas, forms a temporary union with oxygen, which is again given off in the state of gas, when the metal cools spontaneously, or is poured into cold water. This property, it has been shown by Chevillot‡ belongs only to pure silver, and not to silver alloyed even with a very small proportion of copper. H. 2. 133.

Oxide.

1659. *Oxide of silver* may be obtained by adding a solution of baryta to the solution of nitrate of silver, washing the precipitate and heating it to dull redness. It is of a dark olive colour, tasteless, insoluble in water, and when gently heated, is reduced to the metallic state.

The composition of oxide of silver has been very variously given, probably from the difficulty of obtaining it of similar purity. According to Sir H. Davy 100 parts of silver unite with 7,3 oxygen, or according to Dr Wollaston's scale 7,4. A larger proportion of oxygen was formerly assigned by Berzelius; but he has recently given the following statement.

Composition.

| | | | |
|------------------|-------|-----------|-----------|
| Silver | 93,12 | | 100, |
| Oxygen | 6,83 | | 7,3986 |
| | <hr/> | | <hr/> |
| | 100, | | 107,3986† |

Taking the proportion of oxygen which combines with 100 parts of silver at 7,3 the equivalent number for silver will be 110. No other oxide of silver has been actually ascertained to exist; though from the experiments of Mr Faraday, there seems reason to believe that the pellicle, which forms spontaneously on an ammoniacal solution of oxide of silver, exposed to the air, is a protoxide of that metal in which the oxygen is to the silver as 7,5 to 157,4.‖ H. Dr Thomson admits it to be a distinct oxide, and considers it as constituted of 3 atoms of silver + 2 atoms of oxygen.¶

Chloride.

1660. *Silver and Chlorine.*—*Chloride of Silver.*—This compound is easily procured by adding a solution of chlorine, of muriatic acid, or of common salt, to a solution of nitrate of silver: it falls in the form of a heavy insoluble tasteless powder, of a white colour, but which, by exposure to light, becomes brown, and ultimately black. When dry chloride of silver is heated to dull redness in a silver crucible it does not lose weight, but fuses; and, on cooling, concretes into a grey semi-

Eliquation.

* The old process of *eliquation* is now scarcely used; it consisted in fusing alloys of copper and silver with lead; this triple alloy was cast into round masses which were set in a proper furnace, upon an inclined plane of iron, with a small channel grooved out, and heated red-hot, during which the lead melted out, and in consequence of its attraction for silver, carried that metal with it, the copper being left behind in a reddish black spongy mass.—Aikin's Dictionary, Art. Silver.

† Manchester Society's *Memoirs*, N. S. vol. iii.

‡ *Ann. de Chim. et Phys.* xiii, 299.

‖ *Quart. Jour.* iv. 270.

§ *Ann. of Philos.* xv. 93.

¶ *First Principles*, i. 434.

transparent substance, which has been called *horn silver*, or *luna cornea*. If slowly cooled, Proust has remarked that it has a tendency to octoëdral crystallization. Heated to a bright red or white heat in an open vessel, it volatilizes in dense white fumes.

1661. If fused with twice its weight of potassa or soda, chloride of silver is decomposed, and a globule of metallic silver is obtained. It is also rapidly decomposed by tin and zinc. Triturated with zinc filings and moistened, the heat produced is so considerable as to fuse the resulting alloy of zinc and silver.*

Decomposition.

1662. Chloride of silver is very soluble in ammonia, a circumstance by which it is usually distinguished from some other chlorides, which, like it, are white, and formed by precipitation. We should be cautious in applying heat to the ammoniacal solution, as it sometimes forms a precipitate of fulminating silver. The ammoniacal solution furnishes crystals, which, when exposed to air, or put into water, lose their transparency, ammonia is evolved, and they crumble into chloride of silver. The fused chloride, exposed to ammoniacal gas, absorbs a considerable portion, which is given off by heat. If the dry chloride thus saturated with ammonia, be thrown into chlorine the ammonia spontaneously inflames.† Chloride of silver is soluble in and decomposed by all the liquid hyposulphites.

Action of ammonia.

1663. To determine experimentally the composition of chloride of silver, 100 grains of the metal may be dissolved in nitric acid and precipitated by a solution of common salt. The precipitate being carefully washed with water slightly acidulated with nitric acid, dried, and fused, the increase of weight on the silver shows the quantity of chlorine which has been gained. Different chemists have given different statements. Wenzel found that 100 of silver gave 131,4 of chloride; Davy, 132,5; Bucholz, Rose, Marcet, and Gay-Lussac, 133,3, and Berzelius, from several experiments, considers 132,75 as the true product.‡ Taking Sir H. Davy's result, the composition of chloride of silver is

Composition.

| | | | | | |
|--------------------|------|-----------|------|-----------|--------|
| Silver | 75,5 | | 100, | | 307,69 |
| Chlorine | 24,5 | | 32,5 | | 100, |

100.

And the equivalent number for silver, deducible from this analysis, is 110,7, from Berzelius's 109,9. It will perhaps be very near the truth if taken at 110, a number agreeing with that indicated by the composition of the oxide.§ H. 2. 135.

1664. *Chlorate of Silver* is formed by digesting oxide of silver in chloric acid; it forms small rhombic crystals, which,

Chlorate.

* Faraday, *Quarterly Journal of Science and Arts*, viii. 374.

† Faraday, *Quarterly Journal*, v. 75.

‡ *Ann. of Philos.* xv. 93.

§ *Native Chloride of Silver* has been found in most of the silver mines; it occurs massive and crystallized in small cubes.

by the action of chlorine, are converted into chloride of silver.

1665. Muriatic acid has no action upon a piece of clean silver, unless boiled with it for a long time, when a slight crust of chloride forms upon it.

Exp. A beautiful experiment, illustrating the influence of electricity on chemical action, consists in attaching a slip of silver to one of zinc, and putting the double bar into dilute muriatic acid; the silver instantly acquires a crust of chloride, in consequence of the negative energy imparted to it by the zinc, the latter metal being rapidly dissolved.

Silver and
Bromine.

1666. *Bromide of Silver* has the same curdy appearance as the chloride, becomes black by exposure to light, is soluble in ammonia, and insoluble in nitric acid, which does not decompose it even at a boiling temperature. Boiling sulphuric acid, on the contrary, detaches some vapours of bromine. The bromide of silver is decomposed by hydrogen in a nascent state, and was found by M. Balard to consist of silver 589, bromine 411.*

Nitrate.

1667. *Nitrate of Silver*.—Nitric acid diluted with three parts of water, readily dissolves silver, with the disengagement of nitrous gas. If the acid contain the least portion of muriatic, the solution will be turbid, and deposit a white powder; and if the silver contain copper, it will have a permanent greenish hue; or if gold, that metal will remain undissolved in the form of a black powder.†

The solution should be perfectly clear and colourless; it is caustic, and tinges animal substances of a deep yellow, which, by exposure to light, becomes a deep purple, or black stain, and is indelible, or peels off with the cuticle: it consists of reduced silver. It may be obtained in white crystals, of a bitter and metallic taste, and soluble in about their own weight of water at 60°. It blackens when exposed to light, and when thus acted upon, is no longer perfectly soluble in water, owing to the separation of a portion of metallic silver.

Lunar caustic.

1668. When heated in a silver crucible it fuses, and if cast into small cylinders, forms the *lapis infernalis*, or *lunar caustic* of pharmacy; the *argenti nitras* of the *Pharmacopœia*. In forming this preparation, care should be taken not to overheat the salt, and the moulds should be warmed. Exposed to

Iodide.

* *Iodide of Silver* is precipitated upon adding hydriodic acid to a solution of nitrate of silver. It is of a greenish yellow colour, insoluble and decomposed when heated with potassa. It is particularly characterized by insolubility in ammonia.

Todate.

Iodate of Silver is precipitated in the form of a white powder by adding iodic acid or iodate of potassa to a solution of nitrate of silver. It is very soluble in ammonia.

† A very useful solvent of silver has been discovered by Mr Keir of Birmingham. It is formed by dissolving one part of nitre in about eight or ten parts by weight of concentrated sulphuric acid. This compound (which may be called *nitro-sulphuric acid*) when heated to between 100° and 200° F. dissolves one fifth or one sixth its weight of silver, with an extrication of nitrous gas; and leaves untouched, any copper, gold, lead, or iron, with which the silver may be combined. Hence it is a most useful agent in extracting silver from old plated goods. The silver may be recovered from the solution by adding common salt, and the chloride of silver formed may be decomposed by carbonate of soda.

a red heat, the acid is partly evolved and partly decomposed, and metallic silver obtained.*

1669. Sulphur, phosphorus, charcoal, hydrogen, and several of the metals, decompose this nitrate. Action of sulphur, &c.

A few grains mixed with a little sulphur, and struck upon an anvil with a heavy hammer, produce a detonation; phosphorus occasions a violent explosion when about half a grain of it is placed upon a crystal of the nitrate, upon an anvil, and struck sharply with a hammer; and if heated with charcoal, it deflagrates, and the metal is reduced. Exp.

If a piece of silk dipped into a solution of nitrate of silver be exposed while moist to a current of hydrogen gas, it is first blackened, and afterwards becomes iridescent from the reduction of portions of the metal.† Exp.

A stick of clean phosphorus, introduced into a solution of nitrate of silver, soon becomes beautifully incrustated with the metal, which separates upon it in arborescent crystals. A plate of copper occasions a brilliant precipitation of silver, and the copper is oxidized and dissolved by the acid. Exp.

1670. The precipitation of silver by mercury is very slow, and produces a peculiar symmetrical arrangement, called the *arbor Dianæ*. It was first remarked by Lemery. To obtain this crystallization in its most perfect state, the solution should contain a little mercury, and the mercury put into it should be alloyed with a little silver. Arbor Dianæ.

Make an amalgam, without heat, of four drachms of leaf silver with two drachms of mercury. Dissolve the amalgam in four ounces or a sufficient quantity of pure nitric acid of a moderate strength; dilute this solution in about a pound and a half of distilled water; agitate the mixture, and preserve it for use in a glass bottle with a ground stopper. When this preparation is to be used, the quantity of one ounce is put into a phial, and the size of a pea of amalgam of gold, or silver, as soft as butter, is to be added; after which the vessel must be left at rest. Soon afterwards, small filaments appear to issue out of the ball of amalgam, which increase and shoot out branches in the form of shrubs. U. 703. According to Proust all that is required is to throw mercury into nitrate of silver very much diluted. How made.

1671. The alkaline metallic oxides decompose this salt of silver: it is also decomposed by muriatic, sulphuric, phosphoric, and boracic acid. The protosulphate of iron throws down metallic silver when added to a solution of the nitrate: protomuriate of tin forms a grey precipitate, consisting of peroxide of tin and oxide of silver. Decomposition.

1672. Ammonia added to solution of nitrate of silver occasions a precipitate, soluble in excess of the alkali.

1673. Nitrate of silver is of much use, as a test for chlorine, muriatic acid, and their compounds. It is employed for writing upon linen under the name of *indelible* or *marking ink*, and is an ingredient in many of the liquids which are sold for the purpose of changing the colour of hair; but, when thus em- Uses.
Indelible ink.

* Fused nitrate of silver, according to Proust, is composed of

| | | | | |
|-------------|-----------|-----|-----------|----|
| Silver | - - - - - | 64½ | - - - - - | 70 |
| Oxygen | - - - - - | 6½ | - - - - - | |
| Nitric acid | - - - - - | | - - - - - | 30 |
| | | | 100 | |

This statement, however, cannot be correct, as it assigns too large a proportion of oxygen to the oxide, viz 8,6 to 100 grains of silver.

† See Mrs Fulhame's *Essay on Combustion*.

ployed, it should be very much diluted, and used with extreme caution, on account of its corrosive quality.

Effect of light.

1674. White paper, or white leather, when stained with a solution of nitrate of silver, in the proportion of ten parts of water to one of the salt, undergoes no change in the dark : but when exposed to the light of day, it gradually acquires colour, and passes through a succession of changes to black. The common sun-beams, passing through red glass, have very little effect upon it ; yellow and green are more efficacious ; but blue and violet produce the most decidedly powerful effects. Hence this property furnishes a method of copying paintings on glass, and transferring them to leather or paper.*

Exp.

By a similar process, ivory may be covered with silver. Let a slip of ivory be immersed in a dilute solution of pure nitrate of silver, till the ivory has acquired a bright yellow colour. Then remove it into a tumbler filled with distilled water, and expose it to the direct light of the sun. After two or three hours' exposure, it will have become black ; but on rubbing it a little, the surface will be changed into a bright metallic one, resembling a slip of pure silver. As the solution penetrates deep into the ivory, the bright surface, when worn away, is replaced by a succession of others. H. 2. 137.†

Sulphuret.

1675. *Sulphuret of Silver*.—Silver readily combines with sulphur, and produces a very crystallizable compound, considerably more fusible than silver. It is this which forms the *tarnish* upon silver plate. It has been analyzed by Berzelius, and found to consist of

| | | |
|-------------------|------------------|-------|
| Silver | 87,032 | 100 |
| Sulphur | 12,968 | 14.9 |
| | <hr/> | <hr/> |
| | 100, | 114.9 |

1676. Sulphuretted hydrogen and hydrosulphuret of ammonia occasion a copious black precipitate of sulphuret of silver when added to solutions of the metal ; a portion of the silver is frequently at the same time reduced to the metallic state.‡

Hyposulphite.

1677. *Hyposulphite of Silver* has been examined by Mr Herschel in his able paper on the hyposulphurous acid.§ It is formed by dropping a weak solution of nitrate of silver into a very dilute solution of hyposulphite of soda ; a white cloud is at first produced, which re-dissolves on agitation ; on adding more of the precipitant, the cloud re-appears and aggregates into a grey precipitate, which appears to consist of hyposulphite of silver ; the supernatant liquor tastes intensely sweet, which is remarkable considering the disgusting bitterness both of the nitrate and of the hyposulphite.

Hyposulphite of silver is also produced when chloride of silver is dissolved in any of the hyposulphites ; the solution is intensely sweet without any metallic flavour.

Nitrite.

* The process is described by Mr T. Wedgwood, in Nicholson's *Journal*, 8 vo. iii. 167.
† *Nitrite of Silver* is obtained, according to Proust, by long digestion of powdered silver in nitric acid already saturated with the metal. It is more soluble than the nitrate, and difficultly crystallizable. It appears not improbable that this salt may contain the suboxide noticed by Mr Faraday.
‡ For localities, &c. of *Native Sulphuret of silver*, see Cleaveland's *Mineralogy*.
§ *Edin. Philos. Jour.* i. 26.

1678. *Hyposulphite of Potassa and Silver* is formed when liquid potassa is dropped into the solution of chloride of silver in hyposulphite of soda; it separates in the form of a copious precipitate, which, when washed and dried, is found to consist of small grey pearly scales; they are difficultly soluble in water; of a very sweet taste; and heated before the blow-pipe afford a bead of silver.

1679. *Sulphite of Silver* is obtained in crystalline grains by Sulphite. digesting oxide of silver in sulphurous acid.

1680. *Sulphate of Silver* is deposited when sulphate of soda Sulphate. is mixed with nitrate of silver. It is also formed by boiling silver in sulphuric acid. It requires about 90 parts of water at 60° for its solution; in boiling water it is more soluble and is deposited, as the solution cools, in small prismatic crystals: it is decomposed at a red heat. It consists of 1 proportional of oxide of silver, and 1 sulphuric acid.

1681. *Phosphate of Silver* is obtained by dissolving crystals Phosphate. of nitrate of silver in pure water, and adding a solution of phosphate of soda. The neutrality of the nitrate of silver is destroyed, and though the phosphate contains an excess of alkali, the resulting liquor is acid. The precipitate is of a yellow colour. When washed and dried, it is fusible at a red heat without any farther loss of weight. It consists, according to Berzelius,* of

| | | | | |
|-----------------|---------|--------|---------|------------|
| Phosphoric acid | | 17,025 | | 100 |
| Oxide of silver | | 82,975 | | 487,38 |
| | | <hr/> | | |
| | | 100. | | H. 2. 140. |

1682. *Carbonate of Silver* is precipitated in the form of a Carbonate. white insoluble powder, by adding carbonate of potassa to nitrate of silver. It blackens by exposure to light. It consists of

1 proportional of carbonic acid + 1 oxide of silver.

1683. Carbonate of ammonia only throws down a portion of the silver from the nitrate, and forms a triple *ammonio-carbonate of silver*.†

1684. *Fulminating Silver*.—Precipitate nitrate of silver by Fulminating silver. lime-water, and thoroughlyedulcorate and dry the precipitate. Let this be afterward put into a vessel of the purest liquid ammonia, in which it may remain for ten or twelve hours. It will then assume the form of a black powder, from which the fluid is to be decanted, and the black substance left to dry in the air. This is the celebrated compound termed *fulminating silver*,

* *Ann. de Chim. et Phys.* ii. 163.

† *Borate of Silver* is thrown down from the nitrate of silver in the form of white powder, by adding solution of borate of soda. Hydrocyanic acid and hydrocyanate of potassa cause a white precipitate in solutions of silver, which appears to be a cyanide of silver, and which, when heated, gives out cyanogen. *Arsenate of Silver* is precipitated in the form of a white powder, soon becoming yellow and brown by the addition of solution of arsenious acid to nitrate of silver. *Arsenate of Silver* is thrown down from nitrate of silver by arsenic acid, of a reddish brown colour. *Chromate of Silver* is precipitated of a crimson colour by adding chromate of soda to nitrate of silver. It soon loses its brilliant tint and becomes brown.

which explodes with the gentlest heat, and even with the slightest friction. It may be formed, also, by boiling any precipitated oxide of silver, for a few moments, in a mixed solution of potassa and ammonia. The protoxide, however, described by Mr Faraday does not afford it. When once prepared, no attempt must be made to enclose it in a bottle, and it must be left undisturbed in the vessel in which it was dried. Great caution is necessary in the preparation of this substance, for in making experiments on it several fatal accidents have been produced by indiscretion in its use. It even explodes, when moist, on the gentlest friction.*

Detonating
silver.

1685. Another detonating compound of silver, formed by a process similar to that employed in making the fulminating mercury of Mr Howard, has been described by Descotils.† It is prepared by adding alcohol to a heated solution of silver, in nitric acid, while the solution is yet going on. Considerable effervescence arises; the liquor presently becomes turbid; and a heavy, white, crystalline powder falls down. This, when washed and dried, is the *detonating silver*. Heat, a slight blow, or long continued friction, cause it to inflame, with a brisk detonation. Pressure alone is not sufficient unless very powerful. It detonates by the electric spark, and is set on fire with an explosion by concentrated sulphuric acid. Both in the preparation of this substance, and in experiments on its detonation, much caution is necessary; and only very small quantities should be employed. This preparation was originally discovered by Mr E. Howard. In repeating his process Mr Cruickshank dissolved 40 grains of silver in two ounces of strong nitric acid, diluted with an equal weight of water. Then, by heating the solution with two ounces of alcohol, he obtained 60 grains of a white powder, which detonated violently. H.

Liebëg's pro-
cess.

Liebëg prepares it by dissolving a drachm of refined silver in half an ounce of nitric acid sp. gr. 1,52; 2 ounces of alcohol sp. gr. 0,85 are then added, and the whole is gradually raised to ebullition in a matrice. White crystalline flocculi soon appear, and it is then time to discontinue the application of heat. The ebullition, however, continues, and the precipitate increases in quantity. At this time it is important to prevent too rapid cooling, which diminishes the quantity of the product. The proportions of acid and alcohol, also, which have been recommended, are found to answer better than any others.

Fulminating silver, thus prepared, has the form of white silky crystals; it detonates by the smallest shock even under water, by an increase of temperature, or the contact of sulphuric acid; it dissolves in 36 times its weight of boiling water, and separates again on cooling.

Fulminic
acid.

1686. Fulminating silver, it has been shown by Liebëg, contains a peculiar acid, the *fulminic*, which is separated by all alkaline and earthy bases except ammonia, 31,25 per cent. of oxide of silver remaining, all these new compounds are crystallizable, and detonate strongly. A portion of silver seems to

* See Count Rumford's papers, *Phil. Trans.* 1798.

† Nicholson's *Journal*, xviii. 140.

accompany the acid into these combinations, for copper precipitates silver from fulminate of potassa. Indeed a metallic base appears to be necessary to the permanent existence of the acid, whose elements, without such a base, or rather element, appear to be held together by a very feeble attraction. This metallic ingredient differs with the source from which the fulminating compound has been prepared, and it may be either silver, mercury, copper, zinc, or iron.

1687. By decomposing fulminating silver with peroxide of copper, carbonic acid and nitrogen gases were obtained in the same proportions as from the combustion of cyanogen. Of oxide of silver it appears to contain two portions, the one serving as an element of the acid, the other as a base. In 100 parts of the fulminating silver, 38 of oxide fulfil the former function, and 38 the latter. The different *fulminates* all contain a common principle of fulmination independently of their bases, and this common ingredient consists of 1 atom of cyanogen and 1 atom of oxygen, forming *cyanic acid*, which, with a metallic element in addition, constitutes *fulminic acid*. The best way of transferring the fulminic acid from oxide of silver to potassa, is to act upon fulminating silver with chloride of potassium, muriatic acid decomposes fulminating silver and occasions the formation of a new acid, constituted of chlorine, carbon, and azote. Sulphuretted hydrogen, also, passed through a solution of fulminate of silver, causes the production of a new acid, which has the property of changing the colour of perchloride of iron to a deep red. H. 2. 140.

1688. The soluble salts of silver are recognized by furnishing a white precipitate with muriatic acid, which blackens by exposure to light, and which is readily soluble in ammonia, and by affording metallic silver upon the immersion of a plate of copper. The salts insoluble in water are soluble in liquid ammonia, and when heated on charcoal before the blow-pipe, they afford a globule of silver. Salts of silver recognized.

1689. *Chromate of Silver*.—M. Teschemacher obtained crystals of this salt from the solution left after separating the precipitate occasioned by adding nitrate of silver to chromate of potassa. They had a strong metallic lustre, and were of a deep red colour by transmitted light, much resembling native red silver. They were insoluble in cold or hot water, and were reduced by heat to metallic silver and chromic oxide.* Chromate.

1690. *Alloys of Silver*.—The compounds of this metal with potassium, sodium, and manganese, have not been examined. It unites difficultly with iron. Alloys.

1691. When silver and steel are fused together, an alloy is formed, which appears perfect while in fusion, but globules of silver exude from it on cooling, which shows the weak attraction of the metals. At a very high temperature the greater

* *Phil. Mag.* N. S. 1. 345.

part of the silver evaporates, but a portion equal to about 1 in 500 remains, forming a perfect alloy, admirably adapted to the formation of cutting instruments.*

1692. Silver readily combines with zinc and tin, forming brittle alloys. The alloy of silver with copper is of the most importance, as it constitutes plate and coin. By the addition of a small proportion of copper to silver, the metal is rendered harder and more sonorous, while its colour is scarcely impaired. With lead the alloy is grey and brittle, as also with antimony, bismuth, cobalt, and arsenic.†

1693. Amalgam of silver is sometimes employed for *plating*; it is applied to the surface of copper, and the mercury being evaporated by heat, the remaining silver is burnished. The better kind of plating, however, is performed by the application of a plate of silver to the surface of the copper, which is afterwards beaten or drawn out.

Silvering for
dials.

1694. A mixture of chloride of silver, chalk, and pearlash, is employed for silvering brass: the metal is rendered very clean, and the above mixture moistened with water rubbed upon its surface. In this way thermometer scales and clock dials are usually silvered.

Analysis of
alloys.

1695. The analysis of alloyed silver is a very important process, and in continual practice by refiners and assayers. It may be performed in the humid way by dissolving the alloy in nitric acid, precipitating with muriatic acid, and either reducing the chloride by potassa in the way above described (1661), or estimating the quantity of silver which it contains. The usual method, however, which is employed at the mint, and by the refiners, is *cupellation*.

Cupellation.

1696. Of the useful metals, there are only three which are capable of resisting the action of air at high temperatures; these are silver, gold, and platinum; the others, under the same circumstances, become oxidized; it might, therefore, be supposed, that an alloy, containing one or more of the former metals, would suffer decomposition by mere exposure to heat and air, and that the oxidable metal would burn away. This, however, is not the case; for if the proportion of the latter be small, it is protected, as it were, by the former; or, in other cases, a film of oxide coats the fused globule, and prevents the further action of the air. These difficulties are overcome by adding to the alloy some highly oxidable metal, the oxide of which is fusible. Lead is the metal usually selected for this purpose,

* Stodart and Faraday, on the Alloys of Steel. *Quarterly Journal*, ix.—*Boston Jour.* i. 130.

† The standard silver of Great Britain consists of $11\frac{2}{9}$ of pure silver and $\frac{1}{9}$ copper. A pound troy therefore is composed of 11 oz 2 dwts pure silver, and 18 dwts of copper, and it is coined into 66 shillings. B.

The standard silver of the United States consists of 1485 parts of fine silver and 179 parts of copper. The dollar contains 416 grains of standard silver, of which $371\frac{1}{4}$ grains are of pure silver, and 44½ grains of alloy. The Troy pound of standard silver contains 10 oz 14 dwts $4\frac{5}{8}$ grs of fine silver, and 1 oz 5 dwts $19\frac{8}{13}$ grs of alloy; and is coined into $13\frac{1}{3}$ dollars; or, 13 oz of standard silver are coined into 15 dollars.

though bismuth will also answer. Supposing, therefore, that an alloy of silver and copper is to be *assayed*, or analyzed by cupellation: the following is the mode of proceeding.

A clean piece of the metal, weighing about 30 grains, is laminated, and accurately weighed in a very sensible balance. It is then wrapped up in the requisite quantity of sheet lead, (pure and reduced from litharge,) and placed upon a small *cupel*, or shallow crucible, made of bone earth, which has been previously heated. The whole is then placed under the muffle, heated to bright redness; the metals melt, and by the action of the air which plays over the hot surface, the lead and copper are oxidized and absorbed by the cupel, and a button of pure silver ultimately remains, the completion of the process being judged of by the cessation of the oxidation and motion upon the surface of the globule, and by the very brilliant appearance assumed by the silver when the oxidation of its alloy ceases. The button of pure metal is then suffered to cool gradually, and its loss of weight will be equivalent to the weight of the alloy, which has been separated by oxidation. Assaying.

To perform this process with accuracy, many precautions are requisite, and nothing but practice can teach these, so as to enable the operator to gain certain results.*

SECTION XXXVI. Gold.

1697. Gold occurs in nature in a metallic state, alloyed with a little silver or copper, and in this state is called *native gold*. Native. Its colour is various shades of yellow; its forms are massive, ramose, and crystallized in cubes and octoëdra. Large quantities of this metal are collected in alluvial soils and in the beds of certain rivers, more especially those of the west coast of Africa and Peru, Brazil, and Mexico. It is found in various parts of Europe and of North America, especially in North Carolina.†

1698. Gold may be obtained pure by dissolving standard gold in nitro-muriatic acid, evaporating the solution to dryness, re-dissolving the dry mass in distilled water, filtering, and adding to it a solution of protosulphate of iron; a black powder falls, which, after having been washed with dilute muriatic acid and distilled water, affords on fusion a button of pure gold. Method of obtaining pure gold.

1699. Gold is of a deep yellow colour. It melts at a bright red heat, and when in fusion appears of a brilliant green colour. Its specific gravity varies a little according to the mechanical processes which it has undergone; but it may be stated on the average at 19,3. Characters.

* An excellent article upon the subject will be found in Aikin's *Chemical Dictionary*, and in Mr Children's *Translation of Thenard on Chemical Analysis*.

† For an account of the gold mines of North Carolina see *American Journal of Science*, ix. 5.—The quantity of gold from North Carolina deposited for coinage in the U. S. mint, during the year 1827, amounted to about 21,000 dollars in value; the whole amount received to Jan. 7, 1827, was nearly 110,000 and it generally exceeds in fineness the standard of our gold coins.

Gold is so malleable that it may be extended into leaves which do not exceed $\frac{1}{28000}$ th of an inch in thickness. It is also very ductile and considerably tenacious; for a wire only $\frac{78}{1000}$ ths of an inch in diameter will sustain a weight of 150 lbs.

Fusion of
gold.

1700. Gold may be melted by a moderate red heat, *viz.* at about 5237° Fah. The intense heat of a glass-house furnace has no other effect than to keep it in fusion, and even exposure to Mr Parker's powerful burning lens, for several hours, occasioned no loss of weight. After fusion, it crystallizes in short quadrilateral pyramids.

It shows no tendency to unite to oxygen when exposed to its action in a state of fusion; but if an electric discharge be passed through a very fine wire of gold, a purple powder is produced, which has been considered as an oxide.

Action of
acids.

1701. Sulphuric, nitric, and muriatic acids, have separately no evident action on gold; but the last mentioned acid, Proust has observed, by long boiling with finely divided gold, dissolves a small portion. Neither does any acid, of which oxygen is the acidifying principle, except concentrated sulphuric and nitric acids, dissolve the oxides of gold, and even those acids do not form permanent compounds. Nitric acid dissolves it only when heated, and deposits it again in the state of a hydroxide on adding water. Sulphuric acid, on the other hand, dissolves oxide of gold at common temperatures, but decomposes the oxide when heated in contact with it.* H. 2. 144.

Oxides.

1702. *Gold and Oxygen.*—The chemical history of the oxides of gold is as yet very imperfect. Berzelius is of opinion that there are three oxides. The only well known oxide is that which is supposed to exist in the solution of gold combined with muriatic acid. It may be prepared by mixing with a concentrated neutral solution of gold a quantity of pure potassa exactly sufficient for combining with the muriatic acid, a reddish-yellow coloured precipitate subsides, which is rendered anhydrous by boiling, and assumes a brownish black colour.† The best method of forming it, according to Pelletier is by digesting the muriate with pure magnesia, washing the precipitate with water, and removing the excess of magnesia by dilute nitric acid.

1703. The peroxide of gold is yellow in the state of hydrate, and nearly black when pure, is insoluble in water, and is completely decomposed by solar light or a red heat. Muriatic acid dissolves it readily, yielding the common gold solution; but it forms no definite compound with any acid that contains oxygen. It may indeed be dissolved by the nitric and sulphuric acids; but the affinity is so slight that the oxide is precipitated by the addition of water. It combines, on the contrary, with alkaline bases, such as potassa and baryta, apparently forming regular salts, in which it acts the part of a weak acid. These circum-

* Pelletier, *Ann. de Chim. et Phys.* xv. H.

† *Ann. de Chim. et Phys.* xvi. 5.

stances have induced M. Pelletier to deny that the peroxide of gold is a salifiable base, and to contend that the muriatic solution of gold is in reality a chloride of the metal. On this supposition he proposes the term *auric acid* for the peroxide of gold, and to its compounds with alkalies he gives the denomination of *aurates*. T. 443.

1704. Oberkampff* deduces as a mean of three experiments, that 100 parts of gold unite with 10,01 oxygen; Berzelius makes the proportion of the latter at 12,07; and Pelletier, from the composition of the iodide, deduces it to be 10,03. This is assigned as the composition of the peroxide; but besides this, he supposes that there is a protoxide containing only one third of the oxygen which exists in the peroxide. Their composition may, according to Pelletier, be stated as follows:

| | Metal. | Oxygen. | |
|---------------------|--------|---------|------------|
| Protoxide | 100 | 3,3495 | |
| Peroxide | 100 | 10,03 | H. 2. 143. |

Composition
of the oxides.

According to late experiments of Dr Thomson, peroxide of gold consists of 1 atom gold + 3 atoms oxygen; and the muriate consists of 2 atoms muriatic acid, 1 peroxide of gold and 5 atoms of water.†

1705. *Chlorides of Gold*.—The proper solvents of gold are chlorine and nitro-muriatic acid. Oberkampff‡ prefers the former, because a purer solution is obtained, and one which can more easily be freed from excess of acid. Gold leaf, introduced into chlorine gas, takes fire and burns. But if gold leaf be suspended in water, into which chlorine gas is passed, it is dissolved, and the solution may be concentrated by evaporation.

Action of
chlorine.

To dissolve gold in nitro-muriatic acid Vauquelin§ reverses the usual proportions, and mixes two parts by weight of muriatic acid with one of nitric. Three parts of an *aqua-regia* so composed, are equivalent, he finds, to four made with the common proportions.

The solution of gold, in whatever way prepared, has an orange yellow colour; but this Oberkampff finds, is owing to an excess of acid, and it passes to a brownish red, as soon as the redundant acid is neutralized or expelled by heat. The solution should, therefore, be evaporated to dryness, and the dry mass, care being taken not to heat it too strongly, re-dissolved in water. Or, to avoid all risk of decomposition, the liquid may be removed from the fire when sufficiently concentrated to become solid on cooling. The solid obtained has a deep brownish red colour, is very fusible, and readily dissolves in water, giving a reddish yellow solution. The solution Pelletier believes to be a real *chloride*, and not a *muriate*, though occasionally it contains a little free muriatic acid.

* *Ann. de Chim.* lxxx.

† *Edin. Jour.* 182.

‡ 89 *Ann. de Chim.* 140.

§ 77 *Ann. de Chim.* 322.

If, instead of removing the mass from the fire, it be heated still longer, chlorine is disengaged, and a lemon yellow compound is left, which is a *sub-chloride*. By strongly urging the heat, the whole chlorine is expelled, and metallic gold only remains.

According to Pelletier there are two chlorides of gold.

| | Metal. | Chlorine. |
|------------------------------------|--------|-----------|
| The proto-chloride or sub-chloride | = 100 | + 14,715 |
| The per-chloride (soluble) | = 100 | + 44,145 |

It is in the state of per-chloride that gold exists when dissolved by aqua-regia. H. 2. 144.

Gold and
bromine.

1706. *Gold and Bromine*.—Bromine and its aqueous solution dissolve gold. A yellow compound is obtained, which stains animal substances of a violet colour, and is decomposed by heat. According to Lapedius 100 parts contain 50 of gold. It dissolves readily in water, and produces a deep red liquid which yields crystals of hydrobromate of gold: one grain of the crystals colours 5000 grains of water.

Iodine.

1707. The action of *iodine* on gold has been examined by M. Pelletier. When hydriodate of potassa is added to chloride of gold, it produces a very copious yellowish brown precipitate, insoluble in cold water, and easily decomposed by heat. It gave on analysis

| | |
|--------|----|
| Iodine | 34 |
| Gold | 66 |

Triple chlo-
ride of gold
and sodium.

1708. When common salt is added to the solution of gold in nitro-muriatic acid, and evaporated to dryness, a *triple chloride of gold and sodium* is obtained which is the *Auri murias* of the Pharmacopœia. It was first formed by M. Chretien* and has been examined by M. M. Figuier and Berard.† It crystallizes in long four-sided prisms, of a beautiful orange colour, which are not altered by exposure to the air. Its composition is stated by Dr Thomson as follows.

Composition.

| | |
|--------------------|-------------|
| Gold | 25 |
| Chloride of Sodium | 7,5 |
| Chlorine | 9 |
| Water | 9 |
| | <hr/> 50,5‡ |

Fulminating
gold.

1709. A solution of pure ammonia separates, from the solution by nitro-muriatic acid, an oxide of gold, and a portion of ammonia, uniting with the oxide, forms a compound, which detonates very loudly in a gentle heat, and is termed *fulminating gold*.

To obtain this compound, add a solution of ammonia in water, or the pure liquid ammonia, to the dilute solution of gold; a precipitate will appear, which will be re-dissolved if too much alkali be used. Let the liquor be filtered and wash the sediment which remains on the filter with several portions of warm

* See Bigelow's *Sequel*, 52.

† *Jour. de Pharmacie*, vi. 64.

‡ *First Principles*, i. 445.

water. Dry it by exposure to the air, without any artificial heat, and preserve it in a bottle, closed, not with a glass stopper, but merely by a cork.

A small portion of this powder, less than a grain in weight, being placed on the point of a knife and held over a lamp detonates violently. The precise temperature which is required is not known, but it appears to exceed 250° Fahrenheit. At the moment of explosion, a transient flash is observed. Two or three grains, exploded on a pretty strong sheet of copper, will force a hole through it. Neither electricity, nor a spark from the flint and steel, are sufficient to occasion its detonation; but the slightest friction explodes it, and serious accidents have happened from this cause.

This detonation is explained as follows; fulminating gold is an oxide of that metal, combined with ammonia. When its temperature is raised, the ammonia is decomposed; the hydrogen of the alkali unites with the oxygen of the oxide, and reduces the gold to a metallic state; and nitrogen gas, and probably aqueous vapour, are liberated in a highly expanded state. The violent impulse of these æriform products, on the surrounding atmosphere, appears to be the cause of the loud noise that is occasioned by the explosion of this compound. Theory.

1710. The solution of gold is decomposed by many bodies.

Into a dilute solution of gold, contained in a glass jar, put a long narrow slip of charcoal, and expose the whole to the direct light of the sun. The gold will be revived, and will appear on the charcoal in a metallic state, exhibiting a very beautiful appearance. The same change ensues without light, if the solution be exposed to a temperature of 212° . Revival of gold from solutions.

Moisten a piece of white taffeta riband, with the dilute solution of gold, and expose it to a current of hydrogen gas from iron filings, and dilute sulphuric acid. The gold will be reduced, and the riband will be gilt with the metal. By means of a camel's hair pencil, the gold may be so applied as to exhibit regular figures, when reduced. Exp.

The same experiment may be repeated by substituting phosphuretted hydrogen for common hydrogen gas.*

1711. Several of the vegetable acids, but particularly the oxalic, decompose chloride of gold at common temperatures, especially if exposed to the sun's rays. The bin-oxalate of potassa is still more efficient; an effervescence arises from the escape of carbonic acid; and in about an hour all the gold is revived.† Tartaric acid does not produce the same effect, but bi-tartrate of potassa occasions a decomposition, though less rapid. Acetic acid may be mingled with chloride of gold without producing any change. Decomposed by vegetable acids.

1712. Gold is precipitated from its solution in a metallic form, by a solution of green sulphate of iron. This depends on the affinity of the protoxide of iron for a further quantity of oxygen, which takes it from the oxide of gold. Action of iron.

1713. When a sheet of pure tin is immersed in a solution of gold, the oxide of gold is precipitated of a purple colour; and, Purple of Cassius.

* For a detail of various experiments of a similar kind consult an *Essay on Combustion*, by Mrs Fulham; also Count Rumford's paper, in the *Philosophical Transactions*, 1793, page 449.

† Van Mons.

when scraped off and collected, forms the *purple powder of Cassius*, much employed in enamelling. Or the metallic salt, largely diluted with water, may be put into a glass vessel, with a few pieces of grain tin. In a short time the liquor will become of the colour of red wine, and a very light flocculent precipitate will begin to precipitate, leaving the liquor clear. This, when well washed and dried, has a deep purple colour, and is the precipitate of Cassius. The same precipitate is obtained by mixing a solution of gold with a recently made solution of tin in muriatic acid.

1714. The composition and colour of the precipitates of gold, thrown down by muriate of tin at the minimum, have been shown, by Oberkampff, to be variable. The colour approaches more to a violet, as the salt of tin bears a larger proportion to that of gold; and the colour communicated by the precipitate to porcelain, has the same variable character. When the muriate of gold is in excess, the precipitate has more of a rose colour. H. 2. 151.

Ethereal solution of gold.

1715. If a solution of gold be mixed with sulphuric ether it combines with the oxide, and an *ethereal solution of gold* is obtained. Polished steel dipped into this solution acquires a coat of gold, and it has hence been employed for gilding delicate cutting instruments.

Sulphuret.

1716. *Sulphuret of gold* is procured by passing sulphuretted hydrogen through an aqueous solution of gold. It is a black substance, and is a true sulphuret, which gives up its sulphur on the application of heat. It is composed of 1 atom gold, and 3 atoms sulphur.

The sulphuret of gold is soluble in hydro-sulphuret of potassa. Liquid potassa takes up a part, and leaves a yellow powder, which is metallic gold. The alkaline hydro-sulphurets do not dissolve gold, however minutely divided, till sulphur is added, when probably a sulphuret of gold is formed, on which the hydro-sulphuret is capable of acting. H. 2. 151.

Phosphuret:

1717. *Phosphuret of gold* is obtained by heating gold leaf with phosphorus, in a tube deprived of air. It is a grey substance of a metallic lustre, and consists probably of 1 proportional gold + 1 phosphorus.

Equivalent number for gold.

1718. There is still some room for hesitation in fixing upon a number to represent the weight of the atom of gold, on account of the uncertainty respecting the smallest proportions of oxygen, chlorine, &c. with which it is capable of forming a chemical compound. It appears that the only well-ascertained oxide of gold is that which contains, according to Oberkampff, 10.01, and to Berzelius, 12.07 oxygen, on 100 of the metal; and if this be the only oxide, the atom of gold will be represented either by 80, or by 70, as we take the experimental result of the former, or the latter chemist. But if, with Berzelius, we consider this as the *tritoxide*, and view the sulphuret also as a *trito-sulphuret*, the atomic weight of gold will be 198.88,

which very nearly agrees with 200, the number derived by Dr Thomson, as the representative of gold. The whole subject appears, however, to require farther investigation, before an equivalent number can be obtained for gold, entitled to our full confidence. H. 2. 152.

1719. *Alloys of Gold*.—A very curious detail of an extended and accurate series of experiments upon the alloys of gold has been published in the *Philosophical Transactions* for 1803, by Mr Hatchett: his experiments were generally made with 11 parts of gold and 1 of alloy; or 38 grains of alloy to the ounce of gold. Alloys.

1720. The alloys of gold with potassium, sodium, and manganese, have not been examined. With iron the alloy is malleable and ductile, and harder than gold, its colour dull white, and its specific gravity 16,885. The metals expand by union, so that supposing their bulk before combination to have been 1000, after combination it is 1014,7. With potassium, &c.

1721. With zinc the compound is brittle and brass-coloured. Specific gravity 16,937. The metals contract a little in uniting, the original bulk being 1000, that of the alloy is 997. The brittleness continued when the zinc was reduced to $\frac{1}{60}$ th of the alloy. The fumes of zinc in a furnace containing fused gold, make it brittle. — with zinc.

1722. Tin formed a whitish alloy, brittle when thick, but flexible in thin pieces. Specific gravity 17,307. Bulk before fusion 1000; after fusion 981. So that there is considerable contraction. The old chemists called tin *diabolus metallorum*, from its property of rendering gold brittle, but Mr Bingley's experiments, quoted by Mr Hatchett, show that $\frac{1}{60}$ th of tin does not render gold brittle. — with tin.

1723. The alloy of lead is very brittle when that metal only constitutes $\frac{1}{120}$ of the alloy; even the fumes of lead destroy the ductility of gold. The specific gravity 18,080; and 1000 parts become 1005. A very remarkable fact in respect to this alloy is, that its specific gravity diminishes, to a certain extent, as the proportion of lead diminishes, and is at its maximum when the lead amounts only to $\frac{1}{60}$ th part, the quantity of gold remaining the same, and the deficiency being made up with copper.* — with lead.

1724. With copper (standard gold) the alloy is perfectly ductile and malleable, but harder than pure gold, and resists wear better than any other alloy except that with silver. Its specific gravity is 17,157.† Alloys with copper.

* A table exhibiting this remarkable fact has been drawn up by Mr Hatchett. *Phil. Trans.* 1803.

† The gold coin of Great Britain is an alloy of eleven parts of gold and one of copper; of this alloy, twenty troy pounds are coined into 934 sovereigns and one half sovereign; one pound formerly was coined into 44½ guineas; it now produces 462 $\frac{9}{10}$ sovereigns, being melted or alloyed with copper.

The standard of the gold coins of the United States consists of eleven parts of fine gold to one part alloy, which alloy consists of silver and copper in any convenient proportion, provided the silver do not exceed the copper. The eagle of ten dollars contains 270 grains of standard gold, of which 247½ Gold coins of G. Britain.
Gold coins of the United States.

1725. Arsenic and antimony, when alloyed in very small proportions with gold, destroy its colour and render it quite brittle.

Analysis of
alloys of gold.

1726. The analysis of most of the alloys of gold is performed by cupellation. The triple alloy of gold, silver, and copper, may be analyzed by digesting it in nitric acid, which takes up the silver and copper, and leaves the gold in the form of a black powder, which may be fused into a button, and weighed. The silver may be thrown down in the state of chloride by solution of common salt, and the copper precipitated by iron.

Assay.

1727. The assay of gold is more complicated than that of silver, in consequence of the high attraction which it has for copper, and which prevents its complete separation by mere cupellation. An alloy, therefore, of copper with gold, is combined with a certain quantity of silver, previous to cupellation; this is then cupelled with lead in the usual way, and the silver is afterwards separated by the action of nitric acid.

1728. The real quantity of gold or silver taken for an assay is very small; from 18 to 36 grains, for instance, for silver, and from 6 to 12 for gold; whatever the quantity may be it is called the *assay pound*. The silver assay pound is divided into 12 ounces, and each ounce into 20 penny-weights. The gold assay pound is subdivided into 24 carats, and each carat into 4 assay grains.*

Water
gilding.

1729. Mercury and gold combine with great ease, and produce a white amalgam, much used in gilding. For this purpose the amalgam is applied to the surface of the silver; the mercury is then driven off by heat, and the gold remains adhering to the silver, and is burnished. This process is called *water gilding*.

In gilding porcelain, *gold powder* is generally employed, obtained by the decomposition of the chloride; it is applied with a pencil, and burnished after it has been exposed to the heat of the porcelain furnace.

The degree of purity of gold is expressed by the number of parts of that metal, contained in the 24 parts of any mixture. Thus gold, which in 24 such parts (termed *carats*,) contains 22 of the pure metal, is said to be 22 carats fine. Absolutely pure gold, using the same language, is 24 carats fine; and gold alloyed with an equal weight of another metal, 12 carats fine.†

grs. are fine gold, and 22½ grs alloy. The troy pound of standard gold contains 11 oz. of fine gold and 1 ounce of alloy, and is coined into 21½ eagles, of the value of 213½ dollars; or 9 ounces of standard gold are coined into 16 eagles of the value of 160 dollars. The proportional value of fine gold to fine silver by the laws of the United States, is as 15 to 1; so that 1 pound of fine gold is worth 15 pounds of fine silver. The proportional value of the different gold and silver coins is derived wholly from the proportion of fine gold in the one, to the fine silver in the other, the alloy in both being disregarded. Thus 24½ grains of fine gold, being one-tenth of the fine gold in our eagle, are equivalent to our dollar, and multiplied by 15 produce 371¼, the grains of fine silver in the dollar.

* Aikin's Dictionary Article Assay.

† Many curious facts relating to the properties of gold, and its uses in the arts, will be found in Dr Lewis's *Philosophical Commerce of the Arts*.

SECTION XXXVII. *Platinum.*

1730. The original repositories of *native platinum* are not known, it having hitherto been found only in pebbles and grains,* generally small but sometimes upwards of a pound and a half in weight. It is principally found in South America, in the provinces of Choco and Barbacoas, also at Matto Grosso in Brazil. It has also been found in St Domingo,† and in Russia.‡

Native.

The pure metal may be obtained by dissolving crude platinum in nitro-muriatic acid, and precipitating by a solution of muriate of ammonia. This first precipitate is heated, dissolved in nitro-muriatic acid, and again precipitated as before. The second precipitate is heated white hot, and pure platinum remains § It is a white metal. Its specific gravity is 21,5.||

Mode of obtaining.

1731. It is very difficult of fusion, but may be melted by the blow-pipe, with the aid of oxygen gas. A globule weighing 29 grains, boiled violently in the focus of a lens about three feet in diameter;¶ and by means of the oxy-hydrogen blow-pipe more than 200 grains have been kept boiling for some time.

Fused by the blow-pipe.

1732. It is unaltered by the joint action of heat and air. It is very ductile, and may be drawn into wire about the 2000th part of an inch in diameter. It is malleable, and may be beaten into very thin plates, called *platina foil*.

Unaltered by air and heat.

1733. In common with iron, platinum has the property of welding,** which is peculiar to these two metals. It may, also, be united by welding, with iron and steel.

May be welded.

1734. Platinum has been discovered by Dr Wollaston to be a remarkable slow conductor of heat. Its expansion by heat is considerably less than that of steel. From the experiments of Mr Scott of Dublin, it appears to possess sufficient elasticity to be applicable to making of pendulum springs for watches.††

Power of conducting heat.

1735. *Platinum and Oxygen*.—Two oxides of platinum have been described by Berzelius.‡‡ The protoxide is prepared

Oxides.

* Moh's Mineralogy, ii. 441.

† These grains, besides platinum, contain generally gold, iron, lead, palladium, rhodium, iridium, and osmium.

‡ Prof. Osann has discovered three new metals in the Uralian platinum, which have not, however, been named. *Ann. Philos.* Nov. 1827.

§ Various processes have been given for obtaining pure platinum, for which, see Aikin's *Dictionary*, article Platinum; Ure's *Dictionary*, p. 640; *Quart. Jour.* xii. 247. Thenard, *Traite de Chim.* iii. 479, edit. 4.

|| 17,332 (rolled masses) Mohs.

¶ *Ann. de Chim.* lxix. 93

** Two pieces of wrought iron, raised to a white heat, become covered with a kind of varnish; and, when brought into contact, may be permanently united by forging. This is called the welding of iron.

†† Nicholson's *Journal*, xxii. 148.

‡‡ *Ann. de Chim.* 87. 126.

by the action of potassa on the protochloride of platinum. It is of a black colour and consists of

| | | |
|--------------------|-----------------|---------|
| Platinum | 92,35 | 100, |
| Oxygen | 7,65 | 8,287 |
| | <hr/> | <hr/> |
| | 100, | 108,287 |

The peroxide, according to the same chemist, has been obtained only in combination. It is composed of

| | | |
|--------------------|-----------------|--------|
| Platinum | 85,93 | 100, |
| Oxygen | 14,07 | 16,38 |
| | <hr/> | <hr/> |
| | 100, | 116,38 |

Protoxide.

1736. By pouring a neutral proto-nitrate of mercury into a dilute solution of chloride of platinum in hot water, Mr Cooper obtained what he considers the *protoxide of platinum*. The precipitate, a mixture of calomel and protoxide of platinum, after being carefully washed and dried, was exposed to a heat barely sufficient to raise the calomel, after which there remained an intensely black powder. By distillation Mr Cooper ascertained that this powder is composed of 100 parts of platinum + 4,517 oxygen.* It has been objected, however, by Berzelius, and Mr E. Davy, that the temperature required to sublime calomel is sufficient to deprive oxide of platinum of part of its oxygen; and, therefore, that the true composition of the protoxide cannot be determined by Mr Cooper's method.

1737. According to Vauquelin, the oxide of platinum, obtained from the chloride by means of soda is constituted of 100 metal + 15 or 16 oxygen.† H. 2, 155.

Deutoxide of Mr Davy.

1738. Another oxide has been described by Mr E. Davy, which appears to be intermediate between the peroxide, as stated by Berzelius and Vauquelin, and the protoxide of the former chemist. It was formed by boiling together strong nitric acid, and fulminating platinum, drying the product and heating it just below redness; then washing with water, and finally with a little potassa. It was shown by analysis, to contain 96 or 1 atom of platinum, and 12 parts or an atom and a half of oxygen.‡

Chloride.

1739. *Chloride of Platinum*.—Platinum is not acted upon by any other solvents than the nitro-muriatic acid, and chlorine.§ The former is best adapted to effect this solution. Sixteen parts of the compound acid are to be poured on one of the pure laminated metal, and exposed to heat in a glass vessel;

* *Quarterly Journal*, iii.

† *Ann. de Chim. et Phys.* v.

‡ A compound possessing similar properties, has been formed by M. Zeise in the following manner: one part of chloride of platinum, and twelve parts of alcohol of sp. gr. 0,813 are to be put into a retort, and heated slowly until the chloride becomes black, and the liquid clear and colourless. The fluid being decanted, the precipitate is to be washed with warm water until all acid is removed, and then carefully dried. *Bull. Univ. A.* ix. 129.

§ Platinum, by being alloyed with silver and gold, is rendered soluble in nitric acid; 40 *Phil. Mag.* 1; the same fact has been established respecting the alloys of platinum with zinc and copper; *Quart. Jour.* 3. 119.

nitrous gas is disengaged, and a reddish coloured solution is obtained, which gives a brown stain to the skin. When this solution is evaporated, and heated to whiteness, chlorine gas is evolved, and may be collected in a proper apparatus. The dry compound investigated by Mr E. Davy, gave 18,5 per cent. of chlorine.

1740. The solution affords crystals which are very deliquescent and acrid. This solution is distinguished by affording a precipitate upon the addition of muriate of ammonia.

Effect of ammonia.

When this precipitate is heated to redness, the platinum remains in the form of a delicate porous mass, and is the spongy platinum which Professor Døbereiner discovered to possess the property of determining the combination of hydrogen and oxygen. (379.)

The theory of this effect of platinum is very obscure. Døbereiner considers the phenomenon as an electric one, the hydrogen and platinum forming, he supposes, a voltaic combination, in which the former represents the zinc. From the experiments of Dulong and Thenard, it appears that the mixture of atmospheric air, or of oxygen, with the hydrogen gas is necessary to render the platinum incandescent. That metal exerts no action, not even a slow one, on the mixed gases, when in fine powder, nor when laminated or drawn into fine wire; but when beat into the thinnest leaves which it is capable of forming, and especially when rumpled like the wadding of a gun, it was found, by the same chemist, to be efficient at common temperatures. Thicker leaves and wire acted, though slowly, at temperatures between 2 and 300° centig. Gold and silver in very fine leaves were efficient at a heat below that of boiling water, and spongy palladium and iridium inflamed hydrogen at common temperatures. Spongy platinum loses its power after being heated.*

Professor Dana found that spongy platinum is also ignited by the vapour of alcohol or ether.†

1741. According to Dr Thomson, spongy platinum consists of 1 atom of platinum, 2 atoms of chlorine, and 1 atom of sal-ammoniac.‡

Composition.

* *Ann. de Chim. et de Phys.* xxiii. 440.

† *Amer. Jour. &c.* viii. 198.

‡ M. Døbereiner procures this substance by the following process: mix muriate of platinum with neutral tartrate of soda dissolved in water; this mixture is to be heated in a glass tube (about $\frac{1}{2}$ or $\frac{3}{4}$ of an inch in diameter, and 20 to 30 inches in length) until the fluid is rendered slightly turbid, and it is afterwards to be exposed for several days to the sun's rays. The greater part of the platinum is separated from solution, and deposited in the state of minute laminæ of a greyish-black colour, on the sides of the glass. The tube and its contents are to be put into a glass vessel containing water, and it is to be filled with hydrogen gas. The platinum deposited upon the glass becomes almost immediately white and shining like silver. The platinum may be then readily detached from the glass. During the reduction of the platinum, by this process, the tartaric acid is partly converted into carbonic and formic acid. The smaller the laminæ of the metal are, the more readily is the incandescence produced. Spongy platinum (for the lamps for instantaneous light, fig. 86) is prepared of great power by moistening the muriate of ammonia and platinum with a concentrated solution of ammonia; the paste formed is to be heated to redness in an earthen or platinum crucible. Hensmann's *Report de Chim. &c.* Pl. iv.

Soda-muri-
ate.

1742. The solution of platinum forms a triple combination with soda, or *soda-muriate*. This is best obtained by adding to nitric acid, in a retort, platinum, with twice its weight of muriate of soda, and applying heat till about four fifths of the fluid have come over. The remaining liquor forms, on cooling, fine prismatic crystals, sometimes four or five inches long; and either reddish brown, like titanium; yellow like amber, or of a beautiful coquelicot colour.* H. 2. 157.

1743. Ferro-cyanate of potassa affords no precipitate with solution of chloride of platinum. The addition of potassa occasions a precipitate of a triple compound of the alkali and acid.† Sulphuretted hydrogen occasions a black precipitate. Ether separates the oxide of platinum in the same way as that of gold. Muriate of tin occasions a very characteristic red precipitate in very dilute solution of platinum.

Tests.

1744. A solution of platinum, so dilute, as to be scarcely distinguishable from water, assumes a bright red colour, on the addition of a single drop of the recent solution of tin. Professor Silliman recommends hydriodic acid as the best test of platinum. When dropped into a weak solution of that metal it produces a deep wine red colour, or reddish brown, which, on standing becomes very intense.

Sulphurets.

1745. There are, according to Mr E. Davy, three *sulphurets of platinum*. The first, formed by heating the finely-divided metal with sulphur; the second by precipitating nitro-muriate of platinum by sulphuretted hydrogen; and the third, by heating 3 parts of the ammonio-muriate with 2 of sulphur.

1746. According to the same authority there are two *phosphurets*. The first, obtained by heating phosphorus with the metal; the second, by heating phosphorus with the ammonio-muriate of platinum.

Sulphate.

1747. The salts of platinum have been but little examined. Proust and Davy have described a *sulphate*, obtained by acidifying the sulphur in the sulphuret by means of nitric acid. It is of a brown colour, and very soluble; and with soda, potassa, and ammonia, it forms triple salts.

Mr Davy finds the solution of the sulphate in water to be an excellent test for discovering gelatine.

Fulminating
platinum.

1748. Mr E. Davy found that the precipitate by a slight excess of ammonia, when boiled in potassa, washed and dried, was a *fulminating platinum*; it explodes at about 420° , with a very loud report.‡ One grain laid on a thin sheet of copper and exploded produces a report louder than that of a pistol, and the copper is deeply indented. Like fulminating gold, it is incapable of being exploded by percussion.

* *Nicholson's Jour.* 8vo. ix. 67.—According to Dr Thomson, it may be considered either as a compound of

1 atom bichloride of platinum
1 " chloride of sodium
8 atoms of water

Or of 1 atom bi-permuriate of platinum
1 " muriate of soda
5 atoms of water.

† Or *Potassa-muriate*. H.

‡ *Phil. Trans.* 1817.

1749. A very singular compound of platinum is described by Mr E. Davy, in the *Philosophical Transactions*, (1820, p. 108), obtained by mixing equal volumes of strong aqueous solution of the sulphate and of alcohol. The colour of the sulphate slowly disappears, and in some days a black substance subsides, which is washed and dried. It is also formed by boiling the sulphate and alcohol together for a few minutes. This substance is permanent in the air and insoluble in water. It detonates feebly when heated, and is not affected by chlorine, nor by nitric, sulphuric, and phosphoric acids; but it is slowly soluble in muriatic acid. Put into liquid ammonia it acquires fulminating properties, and plunged into the gas it becomes red-hot: the same phenomenon is exhibited by exposing it to the vapour of alcohol, or by placing it upon a piece of paper moistened with that fluid: in these cases the platinum is reduced with the evolution of heat, and the ignition seems to depend upon the slow combustion of the vapour of the alcohol, as has been elsewhere shown. (199). From Mr Davy's analysis of this compound, it appears to contain 96,25 platinum, 0,12 oxygen, 0,0106 carbon, 3,6194 nitric acid and water; the acid being derived from the mode of preparing the sulphate.

1750. The alloys of platinum are not, in general, characterized by useful properties. Its affinity for lead is strikingly shown by the following experiment. Alloys.

If a piece of lead foil, and another of platinum foil, of equal dimensions, be rolled up together, and the flame of a candle be cautiously directed by a blow-pipe towards the edges of the roll, at about a red heat, the two metals will combine with a sort of explosive force, scattering their melted particles and emitting light and heat in a surprising manner.* A small bit of tin, zinc, or antimony, rolled in platinum leaf, and treated in the like manner, exhibits similar appearances. Exp.

1751. Zinc, bismuth, tin, and arsenic, readily combine with platinum, and form fusible alloys. It also unites, though less readily, with copper, lead and iron. It combines with gold, and unless there be great excess of the latter, the colour of the alloy resembles platinum.

1752. By combining 7 parts of platinum with 16 of copper and 1 of zinc, Mr Cooper obtained a mixture much resembling gold.† Sixteen parts by weight of pure platinum, seven parts of copper, and one of zinc equally pure, mixed together in a crucible, and covered with charcoal powder, when perfectly fused, form an alloy which has been called by Dr Hermstadt *artificial gold*. It nearly resembles gold in specific gravity, colour and ductility.

1753. The alloys of steel and platinum have been examined by Stodart and Faraday. They combine in all proportions, but from 1 to 3 per cent. of platinum appears best adapted for cutting instruments. Equal weights of the two metals produce a fine hard and brilliant alloy of a specific gravity of 9,862; it appears Steel and platinum.

* *Ann. of Philos.* xiv. 230.

† *Quart. Jour.* iii. 119.

well adapted for mirrors, for it takes a fine polish and does not tarnish. An alloy of 90 platinum and 20 steel has a specific gravity of 15,88.

1754. Wires of steel and platinum, when welded and polished, exhibit a curious and beautiful surface, especially when the steel parts are slightly acted upon by dilute acid. The welding property of platinum may be usefully applied in the arts; rings may be joined so as to form a chain, the durability of which must add to its value; and with a view to economy, platinum may be joined to iron or steel for many uses in the laboratory of the chemist.

CHAPTER V.

SECTION I. *Chemical Analysis—Of the Analysis of Minerals.*

1755. CHEMICAL analysis consists of a great variety of operations, performed for the purpose of separating the component parts of bodies. In these operations the most extensive knowledge of such properties of bodies as are already discovered must be applied, in order to produce simplicity of effect, and certainty in the results. Chemical analysis can hardly be executed with success, by one who is not in possession of a considerable number of simple substances in a state of great purity, many of which, from their effects are called *reagents*.

As most of the improvements in the science of chemistry consist in bringing the art of analysis nearer to perfection, it is not easy to give any other rule to the learner than the general one of consulting and remarking the processes of the best chemists, such as Scheele, Bergman, Berthollet, Kirwan, Vauquelin, and Berzelius. The bodies which present themselves more frequently for examination than others, are minerals and mineral waters. In the examination of the former, it was the habit of the earlier chemists to avail themselves of the action of fire, with very few humid processes, which are such as might be performed in the usual temperature of the atmosphere. Modern chemists have improved the process by fire, by a very extensive use of the blow-pipe; and have succeeded in determining the component parts of minerals to great accuracy in the humid way. U. 161.

The most common constituents of these compounds are silica, alumina, iron, manganese, lime, magnesia, potassa, soda, and the carbonic and sulphuric acids.

1756. In attempting to separate two or more fixed principles from each other, the first object of the analytical chemist is to bring them into a state of solution. If they are soluble in water,

Object of
chemical
analysis.

Solution.

this fluid is preferred to every other menstruum; but if not, an acid or any convenient solvent may be employed. In many instances, however, the substance to be analyzed resists the action even of the acids, and in that case the following method is adopted:—The compound is first crushed by means of a hammer or a steel mortar, and is afterwards reduced to an impalpable powder in a mortar of agate; it is then intimately mixed with three, four, or more times its weight of potassa, soda, baryta, or their carbonates; and, lastly, the mixture is exposed in a crucible of silver or platinum to a strong heat. During the operation, the alkali combines with one or more of the constituents of the mineral; and, consequently, its elements being disunited, it no longer resists the action of the acids.

i. *Analysis of Marble or Carbonate of Lime.*—This analysis is easily made by exposing a known quantity of marble for about half an hour to a full white heat, by which means the carbonic acid gas is entirely expelled, so that by the loss in weight the quantity of each ingredient, supposing the marble to have been pure, is at once determined. In order to ascertain that the whole loss is owing to the escape of carbonic acid, the quality of this gas may be determined by a comparative analysis. Into a small flask containing muriatic acid diluted with two or three parts of water, a known quantity of marble is gradually added, the flask being inclined to one side in order to prevent the fluid from being thrown out of the vessel during the effervescence. The diminution in weight experienced by the flask and its contents, indicates the quantity of carbonic acid which has been expelled.

Analysis of
marble or
carbonate
of lime.

Should the carbonate suffer a greater loss in the fire than when decomposed by an acid, it will most probably be found to contain water. This may be ascertained by heating a piece of it to redness in a glass tube, the sides of which will be bedewed with moisture, if water is present. Its quantity may be determined by causing the watery vapour to pass through a weighed tube filled with fragments of the chloride of calcium, by which the moisture is absorbed.

The more common kinds of carbonate of lime frequently contain traces of siliceous and aluminous earths, in consequence of which they are not completely dissolved in dilute muriatic acid. A very frequent source of impurity is the carbonate of magnesia, which is often present in such quantity that it forms a peculiar compound called *magnesian limestone*. The analysis of this substance, so far as respects carbonic acid, is the same as that of marble. The separation of the two earths may be conveniently effected in the manner described paragraph 1198.

Separation
of lime and
magnesia.

ii. *Earthy sulphates.*—The most abundant of the earthy sulphates is that of lime. The analysis of this compound is easily effected. By boiling it for fifteen or twenty minutes with a solution of twice its weight of the carbonate of soda, double decomposition ensues; and the carbonate of lime, after being

Earthy sul-
phates.

collected on a filter and washed with hot water, is either heated to low redness to expel the water, and weighed, or at once reduced to quicklime by a white heat. Of the dry carbonate, fifty parts correspond to twenty-eight of lime. The alkaline solution is acidulated with muriatic acid, and the sulphuric acid thrown by the muriate of baryta. From the sulphate of this earth, collected and dried at a red heat, the quantity of acid may easily be estimated.

The method of analyzing the sulphates of strontia and baryta is somewhat different. As these salts are difficult of decomposition in the moist way, the following process is adopted. The sulphate, in fine powder, is mixed with three times its weight of the carbonate of soda, and the mixture is heated to redness in a platinum crucible for the space of half an hour. The ignited mass is then digested in hot water, and the insoluble earthy carbonate collected on a filter. The other parts of the process are the same as the foregoing.

Compounds
of silica, alu-
mina, and
iron.

iii. *Compounds of Silica, Alumina, and Iron.*—Minerals, thus constituted, are decomposed by an alkaline carbonate, at a red heat, in the same manner as the sulphate of baryta. The mixture is afterwards digested in dilute muriatic acid, by which means all the ingredients of the mineral, if the decomposition is complete, are dissolved. The solution is next evaporated to dryness, the heat being carefully regulated towards the close of the process, in order to prevent any of the chloride of iron, the volatility of which is considerable, from being dissipated in vapour. By this operation, the silica, though previously held in solution by the acid, is entirely deprived of its solubility; so that on digesting the dry mass in water acidulated with muriatic acid, the alumina and iron are taken up, and the silica is left in a state of purity. The siliceous earth, after subsiding, is collected on a filter, carefullyedulcorated, heated to redness, and weighed.

To the clear liquid, containing iron and alumina, a considerable excess of a solution of pure potassa is added; so as not only to throw down these oxides, but to dissolve the alumina. The peroxide of iron is then collected on a filter,edulcorated carefully until the washings cease to have an alkaline reaction, and is well dried on a sand bath. Of this hydrated peroxide, forty-nine parts contain forty of the anhydrous peroxide of iron. But the most accurate mode of determining its quantity is by expelling the water by a red heat. This operation, however, should be done with care; since any adhering particles of paper, or other combustible matter, would bring the iron into the state of black oxide, a change which is known to have occurred by the iron being attracted by a magnet.

To procure the alumina, the liquid in which it is dissolved is boiled with sal-ammoniac, when the muriatic acid unites with the potassa, the volatile alkali is dissipated in vapour, and the alumina subsides. As soon as the solution is thus rendered

neutral, the hydrous alumina is collected on a filter, dried by exposure to a white heat, and quickly weighed after removal from the fire.

iv. *Separation of Iron and Manganese.*—A compound of these metals or their oxides may be dissolved in muriatic acid. If the iron is in a large proportion compared with the manganese, the following process may be adopted with advantage. To the cold solution, considerably diluted with water, and acidulated with muriatic acid, carbonate of soda is gradually added, and the liquid is briskly stirred with a glass rod during the effervescence, in order that it may become highly charged with carbonic acid. By neutralizing the solution in this manner, it at length attains a point at which the peroxide of iron is entirely deposited, leaving the liquid colourless; while the manganese, by aid of the free carbonic acid, is kept in solution. The iron, after subsiding, is collected on a filter, and its quantity determined in the usual manner. The filtered liquid is then boiled with an excess of the carbonate of soda; and the precipitated carbonate of manganese is collected, heated to low redness in an open crucible, by which it is converted into the brown oxide, and weighed. This method is one of some delicacy; but in skilful hands it affords a very accurate result. It may also be employed for separating iron from magnesia and lime as well as from manganese.

Separation of
iron and man-
gane-
se.

But if the proportion of iron is small compared with that of manganese, the best mode of separating it is by the succinate of ammonia or soda, prepared by neutralizing a solution of succinic acid with either of those alkalies. That this process should succeed, it is necessary that the iron be wholly in the state of peroxide, that the solution be exactly neutral, which may easily be insured by the cautious use of ammonia, and that the reddish-brown coloured succinate of iron be washed with cold water. Of this succinate, well dried at a temperature of 212° F., 90 parts correspond to 40 of the peroxide. From the filtered liquid the manganese may be precipitated at a boiling temperature by carbonate of soda, and its quantity determined in the way above mentioned. The benzoate may be substituted for the succinate of ammonia in the preceding process.

It may be stated as a general rule, that whenever it is intended to precipitate iron by means of the alkalies, the succinates, or benzoates, it is essential that this metal be in the maximum of oxidation. It is easily brought into this state by digestion with a little nitric acid.

v. *Separation of Manganese from Lime and Magnesia.*—If the quantity of the former be proportionally small, it is precipitated as a sulphuret by the hydrosulphuret of ammonia or potassa. This sulphuret is then dissolved in muriatic acid, and the manganese thrown down as usual by means of an alkali. But if the manganese be the chief ingredient, the best method is to precipitate it at once, together with the two earths, by a fixed

Separation of
manganese
from lime
and magne-
sia.

alkaline carbonate at a boiling temperature. The precipitate, after being exposed to a low red heat and weighed, is put into cold water acidulated with a drop or two of nitric acid when the lime and magnesia will be slowly dissolved with effervescence. Should a trace of the manganese be likewise taken up it may easily be thrown down by the hydrosulphuret of ammonia.

Mode of
analyzing an
earthy mineral
containing
silica, alumina,
manganese, lime,
and magnesia.

vi. *Mode of analyzing an Earthy Mineral containing Silica, Alumina, Manganese, Lime, and Magnesia.*—The mineral, reduced to a fine powder, is ignited with three or four times its weight of the carbonate of potassa or soda, the mass is taken up in dilute muriatic acid, and the silica separated in the way already described. To the solution, thus freed from silica and duly acidulated, carbonate of soda is gradually added, so as to charge the liquid with carbonic acid, as in the analysis of iron and manganese. In this manner the iron and alumina are alone precipitated, substances which may be separated from each other by means of pure potassa. The manganese, lime, and magnesia, may be determined by the processes already described.

Analysis of
minerals containing a fixed
alkali.

vii. *Analysis of Minerals containing fixed Alkalies.*—When the object is to determine the quantity of fixed alkali, such as potassa or soda, it is necessary to abstain from the employment of these reagents in the analysis itself; and the beginner will do well to devote his attention to the alkaline ingredients only. On this supposition, he will proceed in the following manner. The mineral is reduced to a very fine powder, mixed intimately with six times its weight of the artificial carbonate of baryta, and exposed for an hour to a white heat. The ignited mass is dissolved in dilute muriatic acid, and the solution evaporated to perfect dryness. The soluble parts are taken up in hot water; an excess of the carbonate of ammonia is added; and the insoluble matters, consisting of silica, carbonate of baryta, and all the constituents of the mineral, excepting the fixed alkali, are collected on a filter. The clear solution is evaporated to dryness in a porcelain capsule, and the dry mass is heated to redness in a crucible of platinum, in order to expel the salts of ammonia. The residue is the chloride of potassium or sodium.*

In this analysis, it generally happens that traces of manganese, and sometimes of iron, escape precipitation in the first part of

* Sir H. Davy observes, that the boracic acid is very useful in analyzing stones that contain a fixed alkali; as its attraction for the different earths at the heat of ignition is considerable, and the compounds it forms with them are easily decomposed by the mineral acids dissolved in water. His process is as follows: Let 100 grains of the stone to be examined be reduced to a fine powder, mixed with 200 grains of boracic acid, and fused for about half an hour at a strong red heat in a crucible of platinum or silver. Digest the fused mass in an ounce and half of nitric acid, diluted with seven or eight times the quantity of water, till the whole is decomposed; and then evaporate the solution till it is reduced to an ounce and half, or two ounces. If the stone contained silica, it will separate in this process, and must be collected on a filter, and edulcorated with distilled water, to separate the saline matter. The fluid, mixed with all the water that has been passed through the filter being evaporated till reduced to about half a pint, is to be saturated with carbonate of ammonia, and boiled with an excess of this salt, till all that will precipitate has fallen down. The earths and metallic oxides being separated by filtration, mix nitric acid with the clear fluid till it has a strongly sour taste,

the process; and, in that case, they should be thrown down by the hydrosulphuret of ammonia. If neither lime nor magnesia is present, the alumina, iron, and manganese, may be separated by pure ammonia, and the baryta subsequently removed by the carbonate of that alkali. By this method the carbonate of baryta is recovered in a pure state, and may be reserved for another analysis. The baryta may also be thrown down as a sulphate by sulphuric acid, in which case, the soda or potassa is procured in combination with that acid.

The analysis is attended with considerable inconvenience, when magnesia happens to be present; because this earth is not completely precipitated either by ammonia or its carbonate; and, therefore, some of it remains with the fixed alkali. The best mode for effecting its separation, is the following. The carbonate of ammonia is first added, and the phosphoric acid is dropped into the liquid, until all the magnesia is thrown down in the form of the ammoniaco-magnesian phosphate. The excess of phosphoric acid is afterwards removed by the acetate of lead, and that of lead by sulphuretted hydrogen. The acetate of the alkali is then brought to dryness, ignited, and by the addition of sulphate of ammonia is converted into a sulphate.

In the preceding account, several operations have been al-
luded to, which, from their importance, deserve more particular
mention. The process of filtering, for example, is one on which
the success of analysis materially depends. Filtration is effected
by means of a glass funnel, into which a filter (figs. 6 and 17,) of
nearly the same size and form, made of white bibulous paper, is
inserted.* For researches of delicacy, the filter, before being
used, is macerated for a day or two in water acidulated with nitric
acid, in order to dissolve lime and other substances contained
in common paper, and it is afterwards washed with hot water
till every trace of acid is removed. It is next dried at 212° ,
or any fixed temperature insufficient to decompose it, and then
carefully weighed, the weight being marked upon it with a
pencil. As dry paper absorbs hygrometric moisture rapidly
from the atmosphere, the filter while being weighed, should be
inclosed in a light box made for the purpose. When a precipi-
tate is collected on a filter, it is washed with pure water until
every trace of the original liquid is removed. It is subse-
quently dried and weighed as before, and the weight of the
paper subtracted from the combined weight of the filter and
precipitate. The trouble of weighing the filter may sometimes
be dispensed with. Some substances, such as silica, alumina,
and lime, which are not decomposed when heated with com-

Filtration.

Pl. ix.

and then evaporate till the boracic acid remains free. Filter the fluid, evaporate it to dryness, and expose it to a heat of 450° F. when the nitrate of ammonia will be decomposed, and the nitrate of potassa or soda will remain in the vessel. The earths and metallic oxides that remained on the filter, may be distinguished by the common process. The alumina may be separated by solution of potassa, the lime by sulphuric acid and the oxide of iron by succinate of ammonia, the manganese by hydrosulphuret of potassa, and the magnesia by pure soda.

* On this process see Faraday's *Chem. Manip.* sect. ix.

bustible matter, may be put into a crucible while yet contained in the filter, the paper being set on fire before it is placed in the furnace. In these instances, the ash from the paper, the average weight of which is determined by previous experiments, must be subtracted from the weight of the heated mass.

The tests commonly employed in ascertaining the acidity or alkalinity of liquids are litmus and turmeric paper. The former is made by digesting litmus, reduced to a fine powder, in a small quantity of water, and painting with it white paper which is free from alum. The turmeric paper is made in a similar manner; but the most convenient test of alkalinity is litmus paper reddened by a dilute acid.*

SECTION II. *Of the Analysis of Mineral Waters.—Examination of Mineral Waters by Tests.*†

Division of
mineral wa-
ters.

1757. i. The term *mineral water* is applied to those natural spring waters which contain so large a proportion of foreign matter as to render them unfit for common domestic use, and to confer upon them a sensible flavour, and specific action upon

Tests and
Reagents.

* From Turner's *Elements*, p. 682, &c. For many important practical remarks on analysis, see Faraday's *Chem. Manip.* sect. vi. viii. xi. &c. and Henry's *Chem.* 72, 589.

† Those who have not access to a regular laboratory will find it convenient to arrange the following tests and re-agents in the manner represented in plate vi. of this work, the larger phials should contain about 6 ounces by measure; the second size, 3 ounces; and the smallest, 1 ounce. Of these phials, the greater number should be simply stopped, and a few of them provided with an elongated stopper dipping into the fluid which they contain.

The larger phials may contain the following re-agents;

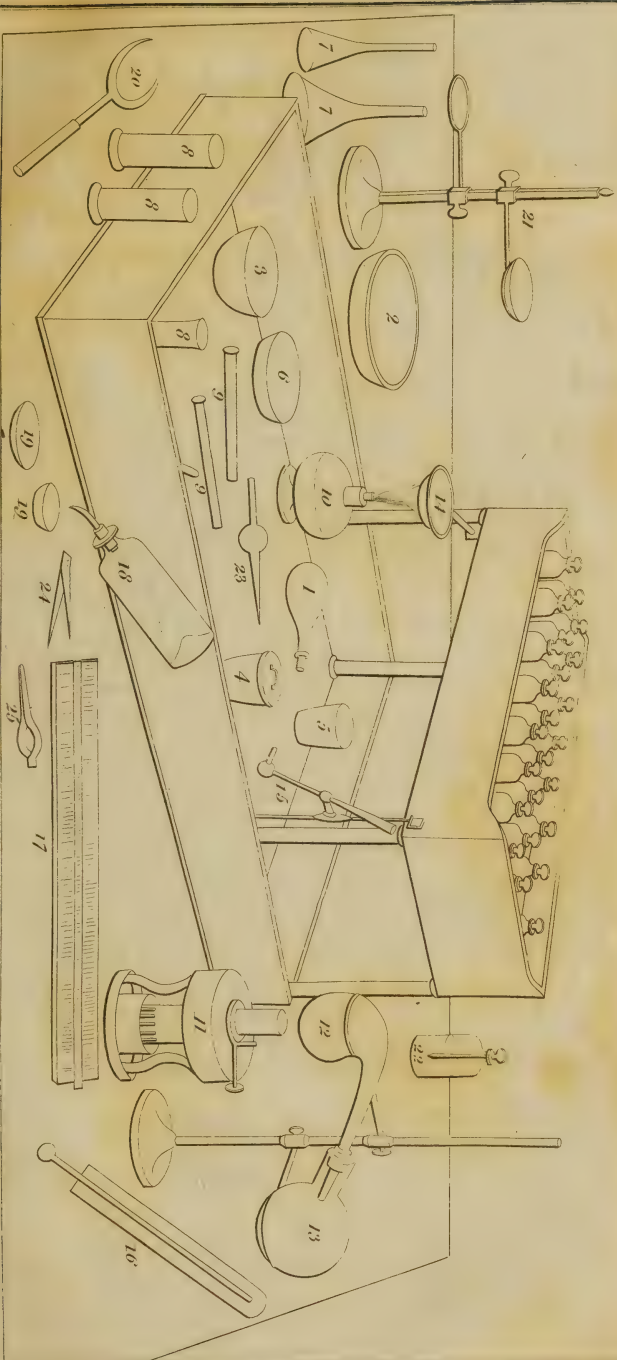
| | |
|--|--------------------------------|
| Pure sulphuric acid. | Solution of carbonate of soda. |
| — nitric acid. | — carbonate of ammonia. |
| — muriatic acid. | — oxalic acid. |
| Dilute sulphuric acid, 1 acid + 3 water. | — oxalate of ammonia. |
| — nitric acid - - - ditto. | — baryta. |
| — muriatic acid - - - ditto. | — acetate of baryta. |
| Solution of potassa. | — nitrate of baryta. |
| — soda. | — phosphate of soda. |
| — ammonia. | — sulphate of silver. |
| — carbonate of potassa. | Alcohol. |

The smaller phials may contain

| | |
|--------------------------------|--|
| Tincture of galls. | Solution of soap in alcohol. |
| Solution of iodine in alcohol. | Phosphorus. |
| — nitrate of silver. | Sulphate of lime. |
| — ferro-cyanate of potassa. | Test-papers, turmeric, litmus, violet. |
| — muriate of lime. | Black flux. |
| — hydrosulphuret of ammonia. | Nitrate of ammonia. |
| — hydriodate of potassa. | |

Portable
laboratory.

The tray should contain a few Florence flasks (1), Wedgwood and glass basins (2, 3), a platinum and a silver crucible (4, 5), silver capsule (6), some funnels (7), test-glasses (8), test-tubes (9), and glass rods, filtering paper a spirit (10), and an Argand's lamp (11), a retort (12), and receiver (13), a copper basin to serve as sand-bath (14), a blow-pipe (15), a thermometer (16), a scale of equivalents (17), a dropping-bottle (18), a few watch-glasses (19), a support for holding glasses over a lamp (20), a small brass stand with rings (21), a tube, with a bulb in the centre and a pointed extremity for drawing up small portions of liquids (23), platinum pincers (24, 25); a small but good balance, with well-adjusted weights, is also requisite, accompanied by a phial and counterpoise for taking specific gravities; and, lastly, a small mercurial trough. There should also be a plentiful supply of distilled water, a portion of which should be contained in a dropping bottle.



Portable Laboratory for the Analysis of Mineral Waters



the animal frame. Their temperature is liable to considerable variation, and is sometimes their principal character, as is the case with the waters of Bath and Buxton; but they are generally so far impregnated with acid or saline bodies, as to derive from them their peculiarities, and in this respect may conveniently be arranged under the heads of *carbonated*, *sulphureous*, *saline* and *chalybeate* waters. The mere taste of the water enables us to determine to which of these subdivisions it probably belongs.

ii. In examining a mineral water, it is of importance to ascertain its specific gravity, which gives us some insight into the proportion of its saline ingredients, its specific weight as compared with pure water, being of course augmented by its foreign contents. Mr Kirwan* has given the following formula for calculating the proportion of saline substances in a water of known specific gravity: "subtract the specific gravity of pure water from that of the water examined, and multiply the remainder by 1,4. The product is equal to the saline contents in a quantity of the water denoted by the number employed to indicate the specific gravity of distilled water. Thus suppose the specific gravity of the water = 1,079, and that of pure water = 1,000, then $79 \times 1,4 = 110,6$ = saline contents in 1000 of the mineral water."

Specific gravity.

This is a useful formula, but open to certain objections; and as it is often of considerable importance to acquire a just knowledge of the proportion of foreign bodies in water, it is advisable to conjoin the above method with the following:

Proportion of foreign bodies how ascertained.

iii. Evaporate a given weight, say, 1000 parts to dryness, and expose the residue for 24 hours to a temperature not exceeding 300° upon a platinum capsule; weigh it while warm, and the mean obtained from this and the former experiment, will give the proportion of dry saline ingredients within an error of two per cent. Thus suppose 1000 parts of the above-mentioned water give by evaporation 114,4 dry residue, then $110,6 \div 114,4 = 225 \div 2 = 112,5$ = quantity of saline matter in a dry state (salts deprived of water of crystallization) existing in the mineral water under investigation.

iv. Having by these preliminary operations ascertained the relative *quantity* of foreign matter in the water under examination, the *nature* of the substances present is next to be inquired into.

1758. The substances which have been found in mineral waters are extremely numerous, but those which ordinarily occur, are the following:

Substances usually met with.

| | |
|------------------------|-----------------------|
| Oxygen. | Carbonate of iron. |
| Nitrogen. | Muriate of magnesia. |
| Carbonic acid. | Sea salt. |
| Sulphuretted hydrogen. | Sulphate of magnesia. |
| Carbonate of lime. | Sulphate of soda. |
| Carbonate of magnesia. | Sulphate of lime. |

* Essay on Mineral Waters, p. 145.

Oxygen and
nitrogen.

a. Oxygen and nitrogen exist in the greater number of spring waters in the proportions constituting atmospheric air; the proportion of nitrogen is, however, not unfrequently predominant. These gases give no peculiar flavour to the water.

Carbonic
acid.

b. Carbonic acid renders mineral waters sparkling and effervescent: it is detected by occasioning a precipitate in aqueous solution of baryta, which dissolves with effervescence in dilute muriatic acid.

Sulphuretted
hydrogen.

c. The presence of sulphuretted hydrogen is known by its peculiar disagreeable smell; by the production of a black precipitate on dropping into the water a solution of nitrate of silver, and by the deposition of sulphur on adding a few drops of nitric acid.

Carbonates.

d. The carbonates are dissolved in the water by excess of carbonic acid, and consequently fall upon its expulsion by boiling. Carbonate of lime and magnesia are deposited in the form of a white precipitate. Carbonate of iron occasions the separation of a rusty brown ferruginous powder, and the water is blackened by a few drops of tincture of galls.

Detection of
iron,

e. Mr R. Phillips, in his analysis of Bath waters, has shown that the delicacy of galls, as a test for iron, is curiously affected by the presence of certain salts: if the iron be in the state of protoxide, its detection is facilitated by salts with a base of lime, and by alkalies; if in the state of peroxide, lime prevents the action of the test. This is well shown by dissolving a *very* minute proportion of proto-sulphate of iron in a glass of distilled water, and adding a drop of tincture of galls, which occasions no immediate discoloration; but a drop of lime water, or other alkali, instantly renders the presence of iron evident; so that the quantity of iron present in a water cannot be correctly judged of by the degree of precipitation occasioned in it by tincture of galls.

f. Ferro-cyanate of potassa is also a good test to show minute quantities of iron in water, by the blue precipitate which it occasions; its action is aided by previously adding two or three drops of nitric acid to the water; but it is an equivocal test compared with galls.

— of chlo-
rides,

g. The presence of muriatic salts and of chlorides, is indicated by a white cloud on adding sulphate of silver.

— of sul-
phates,

h. The sulphates, when present in water, afford a white precipitate on the addition of nitrate of baryta, which is insoluble in nitric acid.

— of lime,

i. Lime is recognised by a white cloud on dropping oxalate of ammonia into the water. A portion of the precipitate collected upon leaf platinum, and heated before the blow-pipe, may be burned into quick-lime.

— of magne-
sia.

k. Magnesia is rendered evident by adding carbonate of ammonia which throws down the lime, and subsequently pouring in phosphate of soda, which, when magnesia is present, carries a portion of it down in the form of a granular precipitate of ammoniaco-magnesian phosphate.

Such are the readiest means of recognising the presence of the various substances that commonly occur, by the action of re-agents or tests; and, having gained such general information, we next proceed to the analysis of the water, in order to ascertain the relative proportions of the gaseous and saline ingredients which it holds dissolved.

SECTION III. *Analysis of Mineral Waters.*

1758. v. To ascertain the relative proportions of the gaseous contents of water with perfect accuracy, is a very difficult undertaking, and rarely necessary; the following method is sufficiently precise in all ordinary cases of analysis. Provide a Florence flask capable of holding rather more than a measured wine-pint, which quantity of the water under examination is to be introduced into it, and a cork carefully fitted to its neck, through a perforation in which is inserted a glass tube one-eighth inch in diameter, rising perpendicularly about 18 inches, and then bent so as to pass conveniently under the shelf of the mercurio-pneumatic apparatus. (Where a sufficiency of mercury cannot be procured, warm water may be substituted, if only carbonic acid be present, and it may be absorbed by transferring the jar containing it to a solution of potassa.) The flask should be placed over an argand lamp, and heat gradually applied till the water fully boils. The gas evolved is to be collected in the usual way, in a graduated jar over quicksilver, and submitted to the following examination:—

To ascertain
the gaseous
contents.

vi. Throw up a small quantity of solution of potassa, which, if carbonic acid be present, will absorb it, and the quantity will be shown by the diminution of bulk.

Carbonic
acid.

vii. Introduce the remaining air, or a portion of it, into a small bent tube, containing a bit of phosphorus; heat it so as to kindle the phosphorus, and note the diminution of bulk when cold. It is proportional to the oxygen present, and if equal to one-fifth of the whole bulk, the gas may be regarded as atmospheric air.*

Oxygen.

viii. If sulphuretted hydrogen be present it may be separated by a strong alcoholic solution of iodine, which rapidly absorbs it, and scarcely takes up more than its own volume of carbonic acid gas. Chlorine, added to a mixture of sulphuretted hydrogen and carbonic acid, will also produce the absorption of the former if a little water be present; but it cannot be conveniently used over mercury.

Sulphuretted
hydrogen.

ix. During the ebullition it not unfrequently happens that a precipitation ensues, indicating that the substances thrown down

Carbonates.
Iron.

* In separating oxygen a solution of nitric oxide in protosulphate of iron may sometimes conveniently be employed, but it does not give so accurate a result as the action of phosphorus.

were dissolved by carbonic acid; and in that case they should be separated upon a filter A, after which the remaining water may be evaporated to dryness in a glazed porcelain basin; the dry residue transferred to a silver capsule, and perfectly desiccated at a temperature not exceeding 500°. B.

The precipitate A may consist of carbonate of lime, of carbonate of magnesia, or of oxide of iron; or it may be a mixture of the three; dissolve it in dilute muriatic acid, and add oxalic acid, which throws down oxalate of lime; separate this by filtration, and saturate the filtrated portion with carbonate of ammonia, which precipitates the peroxide of iron, and having removed this, evaporate the residuary mixture, and expose the dry salt to a red heat in a small platinum capsule; the magnesia, if any were present, will remain; if not there will be no residue, for the oxalic acid and muriate of ammonia will be destroyed and volatilized.

100 parts of oxalate of lime indicate 77 of carbonate of lime.

100 parts of red oxide of iron indicate 90 of black oxide, or 143 of carbonate of iron. When carbonic acid holds iron in solution, the metal is in the state of protoxide, and if air be excluded, it requires long boiling to decompose it; for the same reason, if the water be exposed, under the exhausted receiver of the air-pump, it does not readily become brown, as is the case when it is exposed to air; a drop or two of nitric acid facilitates the deposition of the red oxide.

Magnesia.

100 parts of pure magnesia are equivalent to 213 of carbonate of magnesia.

x. The dry residue B, is to be digested in six or eight parts of boiling alcohol, specific gravity 0,817, which will take up muriate of magnesia, and in some rare cases (where no sulphates are present) muriate of lime. Filter off the alcoholic solution, and wash the residue C, with a little fresh alcohol, which add to the former, and evaporate to dryness D. The dry mass D, exposed for some time to a heat of 500°, is generally pure muriate of magnesia, if it contain muriate of lime, the latter earth may be separated by solution of oxalic acid, in the state of oxalate of lime.

Conversion of
the muriates
into sul-
phates.

It is convenient in some cases, to convert the muriates of lime and magnesia into sulphates, by pouring upon them excess of sulphuric acid, evaporating to dryness, and heating the dry mass red hot. The sulphate of magnesia may then be almost completely separated from the sulphate of lime, by a small quantity of cold water; or a saturated solution of sulphate of lime may be used, which takes up the sulphate of magnesia, and, of course, leaves the sulphate of lime.

The alcohol will also take up a very minute portion of sea-salt, which, however, is too small to require estimation.

xi. The residue C, insoluble in alcohol, may contain sea-salt, sulphate of soda, sulphate of magnesia, and sulphate of lime; digest it in ten parts of boiling distilled water, which, when

cold, will have taken up every thing but sulphate of lime, of which an inappreciable portion only will have been dissolved ; separate the solution into two equal portions, *a* and *b*.

To *a* add nitrate of silver, and wash and dry the precipitate, Sea-salt. which is chloride of silver, and of which 100 parts indicate 41 of sea-salt.

To *b* add acetate of baryta as long as it occasions a precipitate, which is sulphate of baryta, and which is to be separated, dried and weighed. 100 grains are equivalent to 60,5 of sulphate of soda, and to 51 of sulphate of magnesia.

In order to ascertain the quantity of magnesia present, and consequently the quantity of sulphuric acid belonging to it, evaporate the liquid filtered off the barytic precipitate *E* to dryness ; it will contain sea-salt, acetate of soda, acetate of magnesia, and, probably, a portion of the added acetate of baryta ; ignite the dry mass, and wash it to separate the sea-salt and soda ; magnesia, and carbonate of baryta will remain insoluble, upon which pour dilute sulphuric acid ; digest, filter, and evaporate the clear liquor to dryness : it is sulphate of magnesia, Sulphate of magnesia, equivalent of course to the original portion of the salt ; deduct the sulphuric acid contained in it from the whole in the precipitate *E*, and the remainder will give the quantity united to the soda.

xii. To estimate the quantity of sulphate of lime in the water, — of lime. the residue of the evaporation of one pint may be washed with cold saturated solution of sulphate of lime, which will dissolve every thing but that sulphate, and which may thus be obtained and weighed ; or, add oxalate of ammonia to a given quantity of the boiled and filtered water, collect the precipitate, and dry it at a heat of 500°. 100 grains of this oxalate indicate 104 of dry sulphate of lime.

xiii. Such are the general components of mineral waters, and the means of ascertaining their relative quantities. Let us suppose the following results have been obtained, with a view to illustrate the mode of drawing up the analysis. By the process *v*, twelve cubical inches of gas have been expelled during the ebullition of a pint of water. The exposure to solution of potassa has occasioned a diminution of eleven cubical inches, which, it having been previously ascertained that no sulphuretted hydrogen was present, may be considered as carbonic acid. The remaining gas thrown up into a tube containing a portion of phosphorus, and heated, suffers scarcely any diminution, and the phosphorus does not burn : hence it may be regarded as nitrogen. The gaseous contents, therefore, of the water under examination are in the wine-pint—

| | |
|-------------------------|--------------------|
| Carbonic acid | 11 cubical inches. |
| Nitrogen | 1 ditto.* |

* Of this nitrogen, a small portion will probably have been derived from the air in the tube connecting the flask with the pneumatic apparatus ; a little practice soon enables the operator to ascertain when it has been expelled : or it may be received entire, and afterwards deducted from the whole produce.

If sulphuretted hydrogen be present, it is best to have recourse to a separate operation to estimate its quantity; for this purpose collect the gas as before, and throw up into it a small quantity of alcoholic solution of iodine. The absorption denotes the quantity of the gas. (viii.)

xiv. The next step of the operation relates to the examination of the precipitate deposited during ebullition, (ix. A.) Let us suppose the weight of oxalate of lime to be 3 grains, of oxide of iron 1,5 grain, and of magnesia 1 grain; then the above data give

| | Grains. |
|---------------------------------|---------|
| Carbonate of lime | 2,2 |
| Carbonate of iron | 2,4 |
| Carbonate of magnesia | 2,1 |

xv. The alcoholic solution (x.) may be diluted with water and tested by oxalic acid for lime; if absent, evaporate to dryness as directed. Let us suppose the residue to be

Muriate of magnesia 5 grains.

If the quantity of muriate of magnesia be considerable, greater accuracy is ensured by converting it into sulphate, which is done by placing it in a capsule of platinum, pouring upon it sulphuric acid, evaporating to dryness, and heating the dry mass to dull redness: 100 grains of this dry sulphate of magnesia indicate 94 of muriate of magnesia; hence the water under examination would have given 5,35 grains = 5 grains of muriate.

If the alcoholic solution contain muriate of lime, that earth must be previously separated by oxalic acid; and 100 parts of oxalate of lime are equivalent to 85 of dry muriate of lime.

xvi. The aqueous solution of the residue (c. xi.) being divided into two portions, let us suppose the portion *a* xi. to afford 8,5 of chloride of silver, which indicates of sea-salt 3,5 grains = 7 grains in the pint.

xvii. Let us assume, that the precipitate of sulphate of baryta *b* xi. weighs 15 grains, indicating of

Sulphuric acid 5,1 grains.

The process directed in xi. furnishes of

Sulphate of magnesia 3,75 grains,

which contain 2,5 grains of sulphuric acid, and which deducted from 5,1 grains leave 2,6 grains, which are adequate to the formation of

Sulphate of soda 4,65 grains.

So that the pint (the water having been divided into two equal portions) would contain of

Sulphate of magnesia $3,75 \times 2 = 7,5$ grains.

Sulphate of soda $4,65 \times 2 = 9,3$ grains.

xviii. The addition of oxalate of ammonia, or oxalic acid, to a pint of the boiled water (xii.) furnishes a precipitate of 4,7 grains of oxalate of lime, indicating of

Sulphate of lime 5 grains.

xix. To give a general view, therefore, of the components of the mineral water which has thus been examined, we should place them as follows :—

| | | | |
|------------------------------------|-----------|---------------|---------------------------------------|
| One wine pint contains | | | General view of the con- tents. |
| Carbonic acid | | Cubic inches. | |
| Nitrogen | | 11 | |
| | | 1 | |
| Gaseous contents | | 12 | |
| | | Grains. | |
| Carbonate of lime | | 2,20 | |
| Carbonate of iron | | 2,40 | |
| Carbonate of magnesia | | 2,10 | |
| Muriate of magnesia | | 5,00 | |
| Sea-salt | | 7,00 | |
| Sulphate of magnesia | | 7,50 | |
| Sulphate of soda | | 9,30 | |
| Sulphate of lime | | 5, | |
| Aggregate weight of solid contents | | 40,50 | |

xx. Besides the substances now enumerated, and which may be considered as the most frequently occurring ingredients in mineral waters, there are others occasionally present of which the following is an enumeration, with the best methods of detecting them :

a. Carbonate of soda is known to exist in water, when, after having been boiled down to half its bulk, and, if necessary, filtered, it reddens turmeric paper, and restores the blue of litmus reddened by vinegar ; it also affords an effervescent precipitate with nitrate of baryta, soluble in dilute nitric acid. This carbonate is incompatible with the soluble salts of lime.

Muriate of lime may also be used to detect the alkaline carbonates, with which it affords a precipitate of carbonate of lime. Carbonate of soda is distinguished from that of potassa, by the latter affording a precipitate in neutral muriate of platinum, which the former does not. Carbonate of ammonia is obviously discoverable by its smell, when acted on by caustic fixed alkali or lime.

b. Silica is detected by evaporating the water to dryness, and boiling the residue in dilute muriatic acid. The silica, if present, remains as a white powder not altered by a red heat, but instantly fusing with a particle of carbonate of soda.

c. Boracic acid and borax have been found in certain lakes in India, and in some parts of Italy. To detect boracic acid, evaporate to one-eighth the original weight of water, and add carbonate of soda as long as it occasions any precipitate ; boil and filter. The filtered liquor will contain borate of soda, with some other salts of the same basis ; evaporate to dryness in a platinum crucible, and digest the residue in three or four parts of sulphuric acid, diluted with its bulk of water. If boracic acid be present, it will separate in micaceous crystals.

d. Alumina has been found in a few mineral waters in the state of a sulphate. It may be separated by the following process : Evaporate to dryness, digest in alcohol, and re-dissolve

the residue in eight parts of water; filter and add oxalic acid, which throws down lime, and which, being separated, leaves magnesia and alumina in solution. Carbonate of ammonia throws down the alumina and leaves the magnesia.

Pure ammonia throws down both alumina and magnesia. These earths may be separated by solution of potassa, which dissolves the former but not the latter.

Manganese. *e.* Manganese is sometimes found in water, but only in very small proportion, so as not to amount to more than a trace. Dr Scudamore found a trace of manganese in the waters of Tunbridge Wells, and it has never been discovered in larger proportion.

Nitrates. *f.* It has been said that certain nitrates are occasionally present in water, but such solutions can scarcely be called *mineral waters*. If nitrate of lime be present, it will be taken up from the residue of evaporation by alcohol, and may be decomposed by carbonate of potassa, so as to afford carbonate of lime and crystals of nitre.

Lead. *g.* It sometimes happens that water contains lead, which may be detected by evaporation to one-eighth its bulk, adding a few drops of nitric acid, and then hydriodate of potassa, which gives a yellow insoluble precipitate; and hydrosulphuret of ammonia, which forms a deep brown or black cloud. These precipitates may be reduced by heating them before the blow-pipe upon charcoal, mixed with a little black flux.

Vegetable and animal matter. *h.* If vegetable or animal matter be contained in water, it gives it a brown colour, especially when evaporated. It may be destroyed in the dry residue by igniting it with a small addition of nitrate of ammonia.*

Dr Murray's method.

* Dr Murray, of Edinburgh, remarks that all mineral waters are either saline, or may be reduced under that division, by expelling any excess of carbonic acid by heat, expelling or decomposing sulphuretted hydrogen in like manner, or removing iron by appropriate methods. He then gives a general formula for the analysis of mineral waters as follows:

1. Reduce the water by evaporation, as far as can be done without occasioning any sensible precipitation or crystallization.

2. Add to the water, thus concentrated, a saturated solution of muriate of baryta as long as any precipitation is produced, taking care to avoid adding an excess. By a previous experiment, let it be ascertained whether this precipitate effervesces or not with diluted muriatic acid, and whether it is entirely dissolved: if it is, the precipitate is of course carbonate of baryta, the weight of which, when it is dried, gives the quantity of carbonic acid; 100 grains containing 22 of acid. If it do not effervesce, it is sulphate of baryta, the weight of which, in like manner, gives the quantity of sulphuric acid; 100 grains, dried at a low red heat, containing 34 of acid. If it effervesce, and is partially dissolved, it consists of both carbonate and sulphate. To ascertain the proportion of these, let the precipitate be dried at a heat a little inferior to redness, and weighed; then submit it to the action of dilute muriatic acid; after this, wash it with water, and dry it by a similar heat, its weight will give the quantity of sulphate, and the loss of weight that of the carbonate of baryta.—By this operation the carbonic and sulphuric acids are entirely removed, and the whole salts in the water are converted into muriates; it remains, therefore, first to discover and estimate the quantities of the bases present, and then, to complete the analysis, to find the quantity of muriatic acid originally contained.

3. Add to the clear liquid a saturated solution of oxalate of ammonia as long as any turbid appearance is produced. The lime will be thrown down in the state of oxalate. The precipitate being washed, may be dried; but as it cannot be exposed to a red heat without decomposition, it can scarcely be brought to any uniform state of dryness with sufficient accuracy to admit of the quantity of lime being estimated from its weight; it is, therefore, to be calcined with a low red heat, by which it is to be converted into carbonate of lime, 100 grains of which are equivalent to 56 of lime. But as a

CHAPTER VI.

SECTION I. *Vegetable Substances.*

1759. VEGETABLE substances, though distinguished from each other by peculiar characters, present several circumstances of agreement as to chemical properties. Oxygen, hydrogen, and carbon are their principal ingredients, to which a certain proportion of nitrogen is sometimes added; and variations in the proportions, and mode of combination, of these elements, occasion the great diversity, which subsists among the products of the vegetable kingdom. They are all susceptible of decomposition by heat alone; but we cannot always as in bodies of the mineral kingdom, proceed from a knowledge of their components to the actual formation of the substances themselves. It is not probable, indeed, that we shall ever attain the power of imitating nature in these operations. For in the functions of a living plant, a directing principle appears to be concerned,

Principal ingredients.

portion of carbonic acid may be expelled if the heat is raised too high, or a little water retained if it is not high enough, it is proper to convert it into sulphate, by adding sulphuric acid to a slight excess, and then expose it to a full red heat. The dry sulphate of lime will remain, 100 grains of which contain 41.5 of lime.

4. To the clear liquid poured off after the precipitation of the oxalate of lime, heated to 100°, and, if necessary, reduced by evaporation, add a solution of carbonate of ammonia; and immediately drop in a strong solution of phosphoric acid or phosphate of ammonia, entirely free from any impregnation of lime, continuing this addition with fresh portions, if necessary, of carbonate of ammonia, so as to preserve an excess of ammonia in the liquid as long as any precipitation is produced. Let the precipitate be washed: when dried by a heat not exceeding 100°, it is the phosphate of ammonia and magnesia, containing 0.019 of this earth; but it is better to convert it into phosphate of magnesia by calcination for an hour at a red heat: 100 grains, then, contain 40 of magnesia.

5. Evaporate the liquid remaining after the preceding operations to dryness, and expose the dry mass to heat as long as any vapours exhale, raising it towards the end to redness. The residual matter is muriate of soda, 100 grains of which are equivalent to 53.3 of soda and 46.7 of muriatic acid.

6. Combine the elements obtained by the analysis (taking the quantity of muriatic acid existing in the muriate of soda), in binary combinations, according to the known proportions in which they unite: the excess or deficiency of muriatic acid will then appear; and the amount of the excess being subtracted from the quantity of muriatic acid contained in the muriate of soda obtained,—or the amount of the deficit being added to that quantity, the real quantity of muriatic acid will be obtained. To ensure perfect accuracy, it may be proper to estimate directly the quantity of muriatic acid in a given portion of water, by abstracting any sulphuric or carbonic acid by nitrate of baryta, and then precipitating the muriatic acid by nitrate of silver or nitrate of lead. When the quantity is thus found, the quantities of the other ingredients must bear that proportion to it which will correspond with the state of neutralization.

The results of the analysis may always be stated in these three modes:—1. The quantities of the acids and bases. 2. The quantities of the binary compounds, as inferred from the principle that the most soluble compounds are the ingredients. 3. The quantities of the binary compounds, such as they are obtained by evaporation or any other direct analytic operation.—See *Trans. Roy. Society of Edinburgh*, viii. 250; and Thomson's *Annals*, x. 93, 169. vii. 43. vi. 256, 347.

The following analysis of mineral waters may be advantageously consulted by the student, as containing a variety of useful details which are necessarily omitted in the above observations:—*Analysis of the Hot Springs at Bath*, by Richard Phillips, Esq. *Analysis of the Brighton Chalybeate*, by Dr Marcet. *Analysis of the Tunbridge Wells Waters*, by Dr Seudamore. Mr Children's *Translations of Thenard's Essay on Chemical Analysis*, chap. vi. and Faraday's *Chemical Manipulation*, sect. xi. &c.

peculiar to animated bodies, and superior to, and differing from, the cause which has been termed chemical affinity. H.

Proximate
principles of
vegetables.

1760. Every distinct compound which exists ready formed in plants, is called a *proximate* or *immediate principle* of vegetables. Thus sugar, starch, and gum, are proximate principles. Opium, though obtained from a plant, is not a proximate principle; but it consists of several proximate principles mixed more or less intimately with one another.

Proximate
analysis.

1761. The proximate principles of vegetables are sometimes distributed over the whole plant, while at others they are confined to a particular part of it. The methods by which they are procured are very variable. Thus, gum exudes spontaneously, and the saccharine juice of the maple tree is obtained by incisions made in the bark. In some cases a particular principle is mixed with such a variety of others, that a distinct process is required for its separation. Of such processes consists the *proximate analysis* of vegetables. Sometimes a substance is separated by mechanical means, as in the preparation of starch. On other occasions, advantage is taken of the volatility of a compound, or of its solubility in some particular menstruum. Whatever method is employed, it should be of such a nature as to occasion no change in the composition of the body to be prepared.

Ultimate
analysis.

1762. The reduction of the proximate principles into their simplest parts, constitutes their *ultimate analysis*. By this means chemists ascertain the quantity of oxygen, carbon, and hydrogen, present in any compound. The former method of performing this operation was by what is termed *destructive distillation*; that is, by exposing the compounds to a red heat in close vessels, and collecting all the products. So many different substances, however, are procured in this way, such as water, carbonic acid, carbonic oxide, carburetted hydrogen, and the like, that it is almost impossible to arrive at a satisfactory conclusion. A more simple and effectual method was proposed by Gay-Lussac and Thenard in the second volume of their celebrated *Recherches Physico-Chimiques*. The object of their process, which is applicable to the ultimate analysis of animal, as well as of vegetable substances, is to convert the whole of the carbon into carbonic acid, and the hydrogen into water, by means of some compound which contains oxygen in so loose a state of combination, as to give it up to those elements at a red heat.

Gay-Lussac
and Then-
ard's method.

1763. The agent first employed by these chemists was the chlorate of potassa. This substance, however, is liable to the objection that it not only gives oxygen to the substance to be analyzed, but is itself decomposed by heat. On this account it is now very rarely employed in ultimate analysis, the peroxide of copper, likewise proposed by Gay-Lussac and Thenard, having been substituted for it. This oxide, if alone, may be heated to whiteness without parting with oxygen; whereas it

yields oxygen readily to any combustible substance with which it is ignited. It is easy, therefore, by weighing it before and after the analysis, to discover the precise quantity of oxygen which has entered into union with the carbon and hydrogen contained in the substance submitted to examination.

1764. The ultimate analysis of organic bodies is one of the most delicate operations with which the analytical chemist can be engaged. The chief cause of uncertainty in the process arises from the presence of moisture, which is retained by some animal and vegetable substances with such force that it can be expelled only by a temperature which endangers the decomposition of the compound itself. The best mode of drying organic matters for the purpose, is by confining them with sulphuric acid under the exhausted receiver of an air-pump, and exposing them at the same time to a temperature of 212° F.—a method adopted by Berzelius, and for which a neat apparatus has been described by Dr Prout.* Another source of difficulty is occasioned by atmospheric air within the apparatus, owing to the presence of which nitrogen may be detected in the products, without having been contained in the substance analyzed.

Causes of
uncertainty.

1765. But though the ultimate analysis of organic substances is difficult in practice, in theory it is exceedingly simple. It consists in mixing three or four grains of the body to be analyzed with about 200 grains of the peroxide of copper, heating the mixture to redness in a glass tube, and collecting the gaseous products in a graduated glass jar over mercury.† From the

Theory of the
process.

* *Ann. of Philos.* vol. vi. p. 272.

† For the purpose of applying heat to the tube, and obtaining the gaseous products with only a small quantity of mercury, an useful apparatus has been contrived by Dr Prout. fig. 124.

Pl. 7.

Two square upright pillars are morticed into a square tray (*a a* at the bottom of the figure) about $\frac{3}{4}$ ths of an inch deep, and are fixed at the top by brass screws into a flat shelf of wood, 3 inches broad at each end, and 5 in the middle, in which is an oval slit or hole 4 1-2 inches long and 1 1-4 wide, distant 1 3-4 inches from the right hand extremity of the shelf. Below this is another shelf, *b b*, which is moveable by a rack and pinion worked by a small handle, as shown at *f*. Into a shallow cavity in this shelf is fixed a cistern of copper covered with hard varnish (cast iron would be better) and having a deep cylindrical cavity or well at *d*. This, to economize mercury, may occasionally be filled with a plug of wood or cast iron. The cistern may be of any convenient dimensions, as 5 1-2 long by 1 1-2 wide, and in its bottom, an opening is required about 5-8ths of an inch diameter for admitting the glass tube *g g*, which is secured in its place by a perforated cork, and is passed also through the axis of a brass spirit lamp, which, as well as the wick, has a circular hole for the purpose. The lamp is placed on a small shelf, perforated also, and moveable by the rack and pinion. A small mirror of tin, with the concave side downwards, is screwed to the bottom of the cistern, to guard the cork from being burned by the heat of the lamp. At *h* is a turning button with a semicircular notch for securing in an upright position the jar *k*, which should be capable of containing 7 or 8 cubical inches.

Dr Prout's
apparatus.

The tube *g g* being fixed in its place, and the jar *k* filled with and inverted in mercury, the spirit lamp is set as high as its carriage will permit, and lighted. The part of the tube, which is surrounded by the burning wick soon becomes red hot, and gas is evolved. When it ceases to issue, the lamp may be gradually lowered, so as to heat successively the whole of the tube, and then moved upwards to the top. When this has been skilfully performed, the whole of the substance under analysis will be found to have been decomposed; but to insure accuracy, its contents may be taken out, triturated in a mortar, and subjected to a repetition of the same operation. The gases obtained must be exposed to the action of liquid potassa, which will absorb the carbonic acid. In measuring the residue, it will be necessary to equalize the level of the mercury within and without the receiver, by immersing it in the well *d*. The residuary gas will probably be nitrogen only, but it may be assayed for oxygen by nitrous gas as described (469, n.) The gases must of course be either measured at a mean of the barom-

quantity of carbonic acid procured by measure, its weight may readily be inferred; and from this, the quantity of carbonaceous matter is calculated, by recollecting that every 22 grains of the acid contain 16 of oxygen and 6 of carbon.

Quantity of
hydrogen as-
certained,

1766. In order to ascertain the quantity of hydrogen, the gaseous products are transmitted through a tube filled with fragments of the fused chloride of calcium, which absorbs all the watery vapour, and by its increase in weight indicates the precise quantity of that fluid generated. Every nine grains of water thus collected correspond to one grain of hydrogen and eight of oxygen.

Oxygen,

1767. If the quantity of oxygen contained in the carbonic acid and water corresponds precisely to that lost by the oxide of copper, it follows that the organic substance itself was free from oxygen. But if, on the other hand, more oxygen exists in the products than was lost by the copper, it is obvious that the difference indicates the amount of oxygen contained in the subject of analysis.

Nitrogen,

1768. If nitrogen enters into the constitution of the organic substance, it will pass over in the gaseous state, mixed with carbonic acid. Its quantity may be ascertained by removing the carbonic acid by means of a solution of pure potassa.

It need scarcely be observed, that if the analysis has been successfully performed, the weight of the different products, added together should make up the exact weight of the organic substance employed.

Fluids.

1769. In analyzing an animal or vegetable fluid, the foregoing process will require a slight modification. If the fluid is of a fixed nature, it may be made into a paste with the oxide of copper, and heated in the usual manner. But if it is volatile, a given weight of its vapour is conducted over the peroxide of copper heated to redness in a glass tube.

Gay-Lussac
and Then-
ard's classi-
fication.

1770. The constitution of vegetable substances is not yet sufficiently known to admit of their being classified in a purely scientific order. The chief data hitherto furnished towards forming a systematic arrangement, are derived from a remarkable agreement between the composition and general properties of several vegetable compounds, first noticed by Gay-Lussac and Thenard.* From the ultimate analysis of a considerable variety of proximate principles, these chemists draw the three

eter or thermometer, or the proper corrections made for deviations from these standards, as well as from aqueous vapour, by the rules already given page 93, &c.

To collect the water, a separate operation on another portion of the substance is necessary. When this is done, the mercurial cistern may be removed; and such a condensing apparatus substituted as will be obvious to persons conversant with chemical processes. By the apparatus of Dr Prout, a part only of the tube and its contents can be heated at once. This is of little consequence when solid bodies are acted upon; but in the decomposition of liquids, or of solids yielding liquid products, it is desirable to ignite a greater length of the tube at a time. To effect this, Mr Cooper, of Lambeth,† employs a lamp, which appears to be very well adapted to the purpose.

* *Recherches*, vol. ii.

† For an engraving and description of this, see Faraday's *Chem. Manip.* sect. xiv.

following conclusions: 1st, A vegetable substance is always acid, when it contains more than a sufficient quantity of oxygen for converting all its hydrogen into water; 2dly, It is always resinous, oily, or alcoholic, &c. when it contains less than a sufficient quantity of oxygen for combining with the hydrogen; and, 3dly, it is neither acid nor resinous, but in a state analogous to sugar, gum, starch, or the woody fibre, when the oxygen and hydrogen, which it contains, are in the exact proportion for forming water.*

1771. Dr Prout has recently published a paper† on the composition of simple alimentary substances, with remarks on the analysis of organized bodies, in which he has described an improved method of analysis, and detailed several important results.‡ His first object was to devise, if possible, an unexceptionable mode of determining the proportions of the three or four principles, which, with few exceptions, form organic bodies; and after numerous trials, he adopted a method founded upon the following well known principles. When an organic product, containing three elements, hydrogen, carbon, and oxygen, is burnt in oxygen gas, one of three things must happen. i. The original bulk of oxygen gas may remain the same, in which case the hydrogen and oxygen in the substance must exist in it in the same proportions in which they exist in water: or ii. The original bulk of the oxygen may be increased, in which case the oxygen must exist in the substance in a greater proportion than it exists in water; or iii. The original bulk of the oxygen gas may be diminished; in which case the hydrogen must predominate. Hence it is obvious, that, in the first of these cases, the composition of a substance may be determined, by simply ascertaining the quantity of carbonic acid gas yielded by a known quantity of it; while in the other two, the same can be readily ascertained by means of the same data, and by noting the excess or diminution of the original bulk of the oxygen gas employed.

Dr Prout's
experiments.

Dr Prout considers the principal alimentary substances as reducible to three great classes, the *saccharine*, the *oily*, and the *albuminous*, and his paper relates to the first of these. This, with certain exceptions, includes the substances in which, according to Gay-Lussac and Thenard, the oxygen and hydrogen are in the same proportion as in water.§

SECTION II. Gum.

1772. Gum is contained in considerable quantities in the sap of many vegetables, and frequently appears as a spontaneous

* Turner's *Elements*.

† *Philos. Trans.* for 1827, part 2d. and *Ann. of Philos.* N. S. 13 and 14.

‡ A plate and description of Dr Prout's apparatus is given in the *Ann. of Philos.*

§ *Quart. Jour.* N. S. iv. 480.

Properties. exudation. *Gum arabic* may be taken as a specimen of pure gum. Its specific gravity is about 1.4. It has a slightly yellow tint, and is translucent, inodorous, and insipid. It dissolves in water, forming a viscid solution, or *mucilage*, from which it may be obtained in its original state by evaporation; it is insoluble in alcohol, which, therefore, causes a white precipitate in its aqueous solutions; it is also insoluble in ether and oils; it undergoes no change by exposure to air, and its aqueous solution does not ferment, but only becomes slightly sour when kept for a long time.

Mucous acid. 1773. Gum is decomposed by sulphuric and nitric acids: the former produces water, acetous acid, and charcoal; the latter, among other products, converts a portion of the gum into a white acid substance, called the *mucous acid*, and which is analogous to that obtained from sugar of milk, or *saccholactic acid*, under which head its preparation is mentioned: malic and oxalic acids are also formed.

Solvents of gum. 1774. Dilute sulphuric, and muriatic acids, dissolve gum without change. The alkalies, and solutions of the alkaline earths, also dissolve gum, and the addition of acids occasions its partial precipitation without having undergone much apparent alteration. It combines, with a few of the metallic oxides. A strong solution of permuriate of iron, dropped into a concentrated mucilage, forms a brown jelly of difficult solubility. Silicated potassa also occasions a white flaky precipitate in dilute mucilage, and is, according to Dr Thomson, a very delicate test of gum. By mixing caustic ammonia with a boiling solution of gum, and then adding subnitrate of lead, Berzelius obtained a white precipitate (*gummate of lead*) composed of

| | | |
|--------------|-------------------------|------------|
| Composition. | Gum | 61.75 |
| | Oxide of lead | 38.25 |
| | | <hr/> 100. |

The atomic weight of gum, according to Berzelius, is 90—according to Dr Ure, 68.

Pyromucous acid. 1775. Submitted to destructive distillation, gum affords carbonic acid and carburetted hydrogen gases, empyreumatic oil, water, and a considerable quantity of impure acetic acid, once considered as a peculiar acid, and distinguished by the term *pyromucous acid*, but now ascertained to be merely the acetic, holding in solution a portion of essential oil, and some ammonia, which last is disengaged on adding lime.

Other gums. 1776. There are several varieties of gum differing a little from each other. *Cherry-tree gum*, and *gum tragacanth* do not dissolve in cold water, but in other respects their properties resemble those of gum arabic. To these varieties the generic term of *Cerasin* has been given by some chemists.

Vegetable jelly. 1777. What has been termed *vegetable jelly*, is obtained from the recently expressed juice of various acid fruits, by gentle evaporation. It is a tremulous, soft coagulum, almost

colourless after it has been well washed, and of an agreeable sub-acid taste. In cold water it is scarcely soluble, but in hot water it is abundantly dissolved; and when the solution cools, it again assumes a gelatinous form. By long boiling, however, it loses this property of coagulating; hence the necessity, in preparing jelly from certain fruits, of not submitting the expressed juice to protracted ebullition. Its solution in water is precipitated by infusion of galls. It seems probable that jelly is merely gum combined with some vegetable acid; for by exposing it on a sieve, an acid liquor drains off, and a hard transparent gum-like substance remains.

SECTION III. Sugar.

1778. Sugar may be extracted from the juice of a number of vegetables, and is contained in all those having a sweet taste; that which is commonly employed is the produce of the *arundo saccharifera*, or *sugar-cane*, a plant which thrives in hot climates. Its juice is expressed and evaporated with the addition of a small quantity of lime, until it acquires a thick consistency; it is then transferred into wooden coolers, where a portion concretes into a crystalline mass, which is drained and exported under the name of *muscovado*, or *raw-sugar*. The remaining liquid portion is *molasses*, or *treacle*. A gallon of juice yields on an average about a pound of raw sugar.

Preparation.

Molasses.

1779. The juice, which flows spontaneously from incisions made in the American maple-tree, affords a quantity of sugar sufficient to render it a process worth following. The juice of the carrot, the melon,* and still more remarkably of the beet (*beta vulgaris*, Linn.) yield a considerable proportion of sugar. To obtain it from the latter vegetable, the roots, softened in water, are to be sliced, and the juice expressed. It is then to be boiled down, with the addition of a little lime, till about two-thirds remain, and afterwards strained. These boilings and strainings are repeated alternately, till the liquid attains the consistence of sirup, when it is left to cool. The sugar, thus extracted, retains somewhat of the taste of the root; but it may be purified by the operation used for the refining of West-India sugar, and it then loses its peculiar flavour. The quantity obtained varies considerably; but in general it may be stated at between four and five pounds from 100 pounds of the root, besides a proportion of uncrystallizable sirup. In Germany the expense has been calculated at about three pence per pound.†

Varieties of sugar.

From the experiments of Prout,‡ it appears that a coarse sugar may be procured from grapes at a trifling expense. In

* *Quart. Jour. N. S.* 1. 239.

† See Chaptal on the manufacture of sugar in France, *Phil. Mag.* xlviii. 331.

‡ *Nicholson's Journal*, xxi. 356.

apples and pears, in the juice of liquorice, and in some other vegetable juices, sugar exists, but in a state of combination, which prevents it from assuming a crystallized form. In dried grapes, figs, &c. it is often seen as a superficial incrustation.

Animal sugar.
Honey.

1780. *Honey* is also a variety of sugar containing a crystallizable and an uncrystallizable portion; the predominance of one or other of which gives to it its peculiar character; they may be partially separated by mixing the honey with alcohol, and pressing it in a linen bag; the liquid sugar being the most soluble, passes through, leaving a granular mass, which forms crystals when its solution in boiling alcohol is set aside. Honey also frequently contains wax, and a little acid matter.

Properties of
sugar,

1781. Sugar is a white brittle substance, of a pure sweet taste, soluble in its own weight of water at 60°. Boiling water dissolves a considerably larger quantity. This solution is called *sirup*; it is viscid, and furnishes crystals in the form of four and six-sided prisms, irregularly terminated. Sugar is soluble in alcohol, but much more sparingly so than in water.

Action of
acids,

1782. Nitric and sulphuric acids decompose sugar; the former converts it into oxalic acid; the latter evolves charcoal and produces water and acetous acid.

of alkalies,

1783. The alkalies dissolve sugar, and destroy its sweet taste, which re-appears if an acid be added. When, however, the alkalies are left for a long time in the contact of sugar they effect a more important change, becoming carbonated and converting the sugar into gum. From a solution of sugar in lime-water, Mr Daniell obtained crystals of carbonate of lime and a portion of gum. The addition of phosphuret of lime to sirup produces an analogous change.*

of protoxide
of lead,

1784. When protoxide of lead is digested with sugar and water, a portion is dissolved and afterwards separates in the form of a white insipid powder (*saccharate of lead*;) insoluble in water, and composed, according to Berzelius, of

| | |
|-------------------------|-------|
| Sugar | 41,74 |
| Oxide of lead | 58,26 |

100,00

of caloric.

1785. When sugar is exposed to heat it fuses, becomes brown, evolves a little water, and is resolved into new arrangements of its component elements. If suddenly elevated to a temperature of about 505°, it bursts into flame.

Composition.

1786. According to Lavoisier, sugar is composed of 64 oxygen, 28 carbon and 8 hydrogen. The results of the analysis by different chemists are given below.†

* *Journal of Science and the Arts*, vi. 32.

| | Gay-Lussac. | Berzelius. | Prout. | Ure. | Crum. |
|----------------|-------------|------------|--------|-------|-------|
| † Carbon - - - | 42,47 | 44,200 | 39,99 | 43,38 | 41,8 |
| Oxygen - - - | 50,63 | 49,015 | 53,33 | 50,33 | 51,7 |
| Hydrogen - - - | 6,90 | 6,785 | 6,16 | 6,29 | 6,5 |
| | 100 ‡ | 100. | 100. | 100. | 100. |

‡ Or carbon - - - - - 42,47
Oxygen and hydrogen in the same proportion as water - - - - - 57,53

100.

According to the experiments of Dr Prout pure sugar-candy contains 42,85 carbon and 57,15 water.*

1787. *Manna* is an exudation from the *Fraxinus Ornus*, a Manna. species of ash, growing in Sicily and Calabria. It has a sweet and somewhat nauseous taste, and is used in medicine as a mild aperient. The sweetness of manna is owing, not to sugar, but to a distinct principle called *mannite*, which is mixed with a peculiar vegetable extractive matter. It is soluble in water, and in boiling alcohol, the latter solution on cooling deposits pure mannite in the form of minute acicular crystals. Digested in nitric acid, it yields both oxalic and saccharic acids. Its solution in water does not appear susceptible of vinous fermentation.

SECTION IV. Starch.

1788. Starch, or *Fecula*, may be separated from a variety of vegetable substances; it is contained in the esculent grains, and in many roots. The process for obtaining it consists in diffusing the powdered grain or the rasped root in cold water, which becomes white and turbid; the grosser parts may be separated by a strainer and the liquor which passes deposits the starch, which is to be washed in cold water and dried in a gentle heat.

1789. The common process for obtaining the starch of wheat consists in steeping the grain in water till it becomes soft; it is then put into coarse linen bags, which are pressed in vats of water: a milky juice exudes, and the starch falls to the bottom of the vat. The supernatant liquor undergoes a slight fermentation, and a portion of alcohol and a little vinegar is formed, which dissolves some impurities in the deposited starch; it is then collected, washed, and dried in a moderate heat, during which it splits into the columnar fragments which we meet with in commerce, and which are generally rendered slightly blue by a little smalt.

1790. From the analysis of Dr Pearson we learn that 100 parts of the fresh potato root, deprived of skin, afford

| | |
|-----------------|------------|
| Water | 68 to 72 |
| Meal | 32 " 28 |
| | <hr/> |
| | 100 100 |

Process for
obtaining
starch.

The meal is composed of three distinct substances.

| | |
|-------------------------------|-----------|
| Fecula | 15 to 17 |
| Fibrous matter | 8 " 9 |
| Extract or mucilage | 5 " 6 |
| | <hr/> |
| | 28 32† |

* *Quart. Jour. N. S.* iv. 481.

† *Repertory of Arts*, iii. 383. See also analysis of several varieties of potato in *Ann. Philos.* v. 39.

Of rice, starch constitutes, according to Braconnot, from 83 to 85 per cent.*

Properties of starch.

1791. Pure starch is a white substance, insoluble in cold water, but readily soluble at a temperature between 160° and 180°. Its solution is gelatinous, becomes mouldy and sour by exposure to air, and by careful evaporation yields a substance resembling gum in appearance, which is a compound of starch and water. Starch is insoluble in alcohol and in ether, and occasions no precipitate in the greater number of metallic solutions; in solution of subacetate of lead, however, it occasions a copious precipitate. The most characteristic property of starch is that of forming a blue compound with iodine; it may be obtained by adding an aqueous solution of iodine to a dilute solution of starch.

Insoluble in alcohol, &c.

Precipitates oxide of lead.

Forms a blue with iodine.

Sulphuric and nitric acids dissolve starch, and slowly decompose it, or resolve it into new compounds. Dilute nitric acid dissolves it without decomposition, forming a greenish solution, which deposits starch upon the addition of alcohol. It is slowly soluble in muriatic acid, and insoluble in acetic acid.

Soluble in acids.

Unites to potassa.

Precipitated by tannin.

Potassa, triturated with starch, forms a compound which is soluble in water.

Infusion of galls occasions a precipitate in the solutions of starch, which re-dissolves by heating the liquid to 120°. This property Dr Thomson considers as characteristic of starch.

1792. The change of starch into sugar is always observed during the germination of seeds, and in the process of *malting* a similar conversion is effected.

Malt.

Malt is barley which has been made to germinate to a certain extent, after which the process is stopped by heat. The barley is steeped in cold water, and is then made into a heap or *couch*, upon the malt-floor: here it absorbs oxygen and evolves carbonic acid; its temperature augments, and then it is occasionally turned to prevent its becoming too warm. In this process the radicle lengthens, and the plume, called by the maltsters the *acrospire*, elongates; and when it has nearly reached the opposite extremity of the seed, its further growth is arrested by drying at a temperature slowly elevated to 150° or more. The malt is then cleansed of the rootlets.

Hordein.

1793. Proust has discovered in barley, besides the ingredients of wheat, a peculiar substance, nearly resembling saw-dust in its external characters, to which he has given the name of *hordein*. This substance may be separated from starch by the action of hot water, in which it is quite insoluble. During the process of malting, its proportion is considerably diminished, and it appears to be partly converted into sugar, or into

* *Ann. de Chim. et Phys.* iv. 383.

starch, as will appear from the comparative analysis of malted and unmalted barley given below.*

1794. It appears, then, that the formation of malt consists in the increase of gum, sugar, and starch; and the diminution of gluten and hordein. The starch, that remains after malting, is found changed in its properties; for it does not as before yield a viscid paste, capable of gelatinizing on cooling.

The loss of weight, sustained by grain in malting, which Proust states at one-third, Dr Thomson asserts is greatly over-rated, and that it did not on an average of 50 processes, carried on under his inspection, exceed one-fifth. The hordein of Proust, he considers as starch under some modification, which is changed, by malting, partly into true starch, and partly into sugar. H.

1795. Another mode of converting starch into sugar was discovered by M. Kirchoff; it consists in boiling it with very dilute sulphuric acid. A pound of starch may be digested in six or eight pints of distilled water, rendered slightly acid by two or three drachms of sulphuric acid. The mixture should be simmered for a few days, fresh portions of water being occasionally added to compensate for the loss by evaporation. After this process the acid is saturated by a proper proportion of chalk, and the mixture filtered and evaporated to the consistence of sirup; its taste is sweet, and, by purification in the usual way, it affords crystallized sugar. M. M. de la Rive and Saussure have shown that the contact of air is unnecessary in the above process; that no part of the acid is decomposed, no gas evolved, and that the sugar obtained exceeds by about one-tenth, the original weight of the starch. M. de Saussure, therefore, concludes that the conversion of starch into sugar depends upon the solidification of water.† The starch from wheat, according to the analysis of Gay-Lussac and Thenard is composed, in 100 parts of

Conversion of starch into sugar by sulphuric acid.

Analysis of starch.

| | |
|----------|-------|
| Carbon | 43,55 |
| Oxygen | 49,68 |
| Hydrogen | 6,77 |

Berzelius has given the following as the component parts of starch.‡

| | |
|----------|--------|
| Carbon | 43,481 |
| Oxygen | 48,455 |
| Hydrogen | 7,064 |
| 100,000 | |

1796. Amyline (called amyline by Saussure) is intermediate between gum and starch. It is soluble in boiling water,

Amyline.

| | | In 100 parts of barley. | In 100 parts of malt. | | |
|---------|-----------|-------------------------|-----------------------|----|------------|
| * Resin | - - - - - | 1 | - - - - - | 1 | H. 2. 259. |
| Gum | - - - - - | 4 | - - - - - | 15 | |
| Sugar | - - - - - | 5 | - - - - - | 15 | |
| Gluten | - - - - - | 3 | - - - - - | 1 | |
| Starch | - - - - - | 32 | - - - - - | 56 | |
| Hordein | - - - - - | 55 | - - - - - | 12 | |

† Thomson's *Annals*, vol. ii.

‡ Thomson's *Annals*, vol. v.

and the solution yields by evaporation a pale semi-transparent brittle substance, insoluble in alcohol, but soluble in ten times its weight of cold water, and to any amount in water at 144°. The solution is coagulated into a white paste by sub-acetate of lead. When treated with iodine, it assumes a blue colour. It is precipitated by barytic water, but not by fixed alkalies, by lime water, nor by infusion of galls. H. 2. 262.

British gum.

1797. When starch is exposed to a temperature between 600° and 700° it swells, and exhales a peculiar smell; it becomes of a brown colour, and in that state is employed by calico-printers under the name of *British gum*. It is soluble in cold water, and does not form a blue compound with iodine. Vauquelin found it to differ from gum in affording oxalic instead of mucous acid, when treated with nitric acid.

Other varieties.

1798. Besides the starch of the cerealia and potatoes, the following varieties of this substance are also met with.

- i. *Arrow-root*, the fecula of the *Marantha Arundinacea*.
- ii. *Sago*, extracted from the pith of several species of palm, growing in the East-India islands.
- iii. *Tapioca* and *Cassava*, prepared from an American plant, the *Iatropa Manihot*.
- iv. *Salop*, obtained from the roots of several species of *Orchis*.

Starchy lignin.

1799. *Starchy lignin*.—When the residue of the spontaneous decomposition of starch has been washed successively with cold and hot water, with alcohol, and with diluted sulphuric acid, an alkaline ley, containing $\frac{1}{2}$ th its weight of potassa, still takes up a further portion. From this solution, diluted sulphuric acid precipitates a light brown combustible substance having the appearance of jet. It gives a blue colour to the aqueous solution of iodine, a property which, together with its solubility in a weak alkaline liquor, distinguishes it from common lignin. It is not impossible, however, that the effect may depend on the presence of a small quantity of starch. H. 2. 263.

SECTION V. *Gluten*.

1800. Gluten may be obtained from wheat-flour, by forming it into a paste and washing it under a small stream of water. The starch is thus washed away, and a tough elastic substance remains, which is gluten.

Properties.

Its colour is grey, and, when dried, it becomes brown and brittle. It is nearly insoluble in water and in ether. When allowed to putrefy it exhales an offensive odour, and when submitted to destructive distillation, it furnishes ammonia, a circumstance in which it resembles animal products. Most of the acids and the alkalies dissolve it.

1801. Gluten is an essential ingredient in wheat-flour, and contributes much to its nutritive quality; and gives considerable tenacity to its paste.

According to M. F. Marcet gluten consists of carbon 55,7—oxygen 22,0—hydrogen 7,8—azote 14,5.*

1802. A substance, much resembling gluten, has been found in the juices of certain vegetables, especially in those which are milky and coagulable by acids. It is contained in the sap of the house-leek, of the cabbage, and most of the cruciform plants. Submitted to destructive distillation, it affords ammonia, and is in other respects similar to the animal principle, called albumen; hence it has been termed *vegetable albumen*.

Vegetable
albumen.

1803. The principles which have now been adverted to, viz. sugar, starch, gum or mucilage, and gluten, constitute the principal nutritive ingredients in most of the esculent vegetables. Wheat grown in Great Britain contains from 18 to 24 per cent. of gluten, the remainder being principally starch. The wheat of the south of Europe generally contains a larger quantity of gluten, and is therefore more excellent for the manufacture of macaroni, vermicelli, and other preparations requiring glutinous paste. The excess of gluten in wheat-flour compared with other grain, renders it peculiarly fit for making bread; for the carbonic acid, extricated during the fermentation of the paste, is retained in consequence of its adhesiveness, and forms a spongy and light loaf.†

1804. M. Taddei has given an account of two new principles which he supposes he has found in gluten, and which he has named *gliadine* and *zymome*. Berzelius has very recently made some experiments on gluten, and infers that Taddei had only given two new names to the known and common principles of plants, particularly the seeds of the *gramineæ*.

Gliadine and
zymome;
Berzelius's
experiments.

If gluten be boiled in alcohol, as long as this fluid grows turbid on cooling, a considerable portion of the mass is separated; if water be added to this solution, and the mixture be distilled, the watery fluid remaining in the retort deposits on cooling a coherent glutinous matter, perfectly resembling gluten. This is *vegetable gelatin*, the gluten, of the same nature as the matter separated from rye and barley.

1805. The matter insoluble in alcohol, whilst moist is semi-transparent, and so much like animal albumen, that it is impossible to distinguish by its appearance only, that it is *vegetable*

* *Ann. de Chim. et de Phys.* xxxvi. 27

† A hundred parts of barley contain upon an average 80 parts of starch, 6 of gluten, and 7 of sugar, the remaining 7 parts being husk. From 100 parts of rye Sir Humphry Davy obtained 61 parts of starch and 5 of gluten. From 100 parts of oats he procured 59 of starch, 6 of gluten, and 2 of sugar. 100 parts of peas afforded about 50 of starch, 3 of sugar, 4 of gluten, and a small portion of extractive matter. 100 parts of potatoes yield, upon an average, 20 parts of starch; they may be considered in general as containing from one-fourth to one-fifth of their weight of nutritive matter. The turnip, carrot, and parsnip, chiefly contain sugar and mucilage: 1000 parts of common turnips give about 34 of sugar, and 7 of mucilage; 1000 parts of carrots furnish about 95 of sugar, and 3 of mucilage; and the same quantity of parsnips afford 90 of sugar and 9 of mucilage. The loss of weight in the above cases is referable to water, and inert vegetable matter possessed of the properties of woody fibre.

albumen. Caustic alkali, when the solution is weak and cold, dissolves vegetable albumen, and leaves the filaments of starch which it has retained.

Properties of
vegetable
albumen.

1806. Vegetable albumen is of a yellowish grey colour, adhesive, glutinous and very elastic; it has no taste, but it has a peculiar smell. In a dry atmosphere it becomes shining on the surface, and gradually dries into a mass of a deep yellow colour, and is perfectly transparent, resembling dry animal matter. It dissolves in alcohol, and the solution is of a pale yellow colour, and remains after the evaporation of the spirit, in the form of transparent yellow varnish.

1807. When vegetable gelatine is treated with cold alcohol, a milky fluid is obtained, and a viscid, white matter remains. This matter is not vegetable gelatine and has not been examined; it is dissolved by boiling, but the liquor becomes milky on cooling.

Action of
alkalies,

1808. Vegetable gelatine combines with the caustic alkalies, and when the gelatine is in excess, a solution is obtained, which is so perfectly neutral that no alkaline taste remains. Ammonia and lime water precipitate it from solution in acids and redissolve it. With the earths and metallic oxides it forms insoluble compounds.

of tannin.

1809. The gelatine, in the solid state, is *tanned* exactly like animal gelatine. When dissolved to saturation in weak alkaline solutions, it possesses in so great a degree the properties of white of egg, that it has been mistaken for it.*

Caoutchouc.

1810. *Caoutchouc*, or *Elastic gum* is the concrete juice of the *Hævea caoutchouc* and *Iathropa elastica*, natives of South America, and of the *Ficus Indica* and *Artocarpus integrifolia*, which grow in the East Indies. It is a soft yielding solid, of a whitish colour when not blackened by smoke, possesses considerable tenacity, and is remarkable for its elasticity. It is inflammable, and burns with a bright flame. When cautiously heated, it fuses without decomposition. It is insoluble in water and alcohol; but it dissolves, though with some difficulty, in pure ether. It is very sparingly dissolved by the alkalies, but its elasticity is destroyed by their action. It is decomposed by sulphuric and nitric acids, the former causing a deposition of charcoal, and the latter a formation of oxalic acid.

Solvents.

1811. Caoutchouc is soluble in the essential oils, in petroleum, and in cajeput oil, and may be procured by evaporation from the two latter without loss of its elasticity. The purified naphtha from coal tar dissolves it readily, and as the solvent is cheap, and the properties of the caoutchouc are unaltered by the process, the solution may be conveniently employed for forming elastic tubes, or other apparatus of a similar kind. It is used by Mr Mackintosh of Glasgow for covering cloth with a thin stratum of caoutchouc, so as to render it impermeable to moisture. This property of coal naphtha was discovered by Mr Syme.†

* Berzelius, in *Ann. de Chim.* Feb. 1828.

† *Ann. Philos.* xii.

1812. The composition of caoutchouc according to Dr Ure is Analysis.
90 carbon, 0,88 oxygen and 9,12 hydrogen in 100 parts. From its yielding ammonia when heated in close vessels it probably contains nitrogen. T.

SECTION VI. *Extractive Matter, Lignin, &c.*

1813. The term *extract*, or *extractive principle* has been applied to a peculiar principle which is supposed to form the basis of all the vegetable extracts which are generally made by digesting vegetable substances in water, and evaporating the solution to a solid consistence.

1814. The existence of a distinct principle, under this name has been doubted by M. Thenard, Dr Bostock and Dr Ure; and it is not improbable that future discoveries may resolve it into other known bodies.

1815. It is said to possess the following properties. Properties. It is soluble in water, and the solution is of a brown colour. It is insoluble in ether, but it is soluble in alcohol containing a small portion of water. By repeated solutions and evaporations it may be rendered scarcely soluble in water. Solutions of chlorine of many of the acids, and of most of the metallic oxides, occasion precipitates in the aqueous solution of extractive.

1816. The following substances may be considered under this head, though some of them are obviously widely different from extractive matter.

1817. *Ulm.*—This substance was first noticed by Klaproth, Ulm. spontaneously exuding from the elm. From the observations of Berzelius, it exists in the bark of many other trees, and may be obtained by digestion in alcohol and cold water; and then digesting the residue in water which contains an alkaline carbonate in solution. On neutralizing the alkali with an acid, the ulmin is precipitated.

Ulm is of a dark brown colour, with scarcely any taste or smell. It is sparingly soluble in water and in alcohol, but readily soluble in a weak solution of carbonate of potassa. Very few of the metallic salts occasion a precipitate in its solution. The exudation from the elm is generally combined with carbonate of potassa, and is therefore readily soluble in water. From late experiments Dœbereiner considers it probable that ulmin consists of an atom of oxide of carbon, and an atom of water. Characters.

1818. *Polychroite.* This term has been applied to the Polychroite. extract of saffron.† It is of a deep yellow colour, deliquescent, readily soluble in water and in alcohol, but insoluble in pure sulphuric ether. Exposure to the solar rays soon destroys the

* *Quart. Jour.* ix. 353.

† *Ann. de Chim.* lxxx.

colour of its aqueous solution. Sulphuric acid renders it blue, and nitric acid green: solutions of lime and baryta produce yellow and red precipitates; subacetate of lead throws down a deep yellow precipitate, and nitrate of mercury separates a red powder.

Hematin.

1819. *Hematin*.—This peculiar substance was first recognised by Chevreul in the colouring matter of *log-wood*.* It may be obtained by digesting log-wood in water of the temperature of 125°. Filter, evaporate carefully to dryness, and digest the residue for 24 hours in alcohol of the specific gravity of .837. Filter the alcohol; concentrate the solution by evaporation, add a portion of water, evaporate a little further, and set the solution aside: crystals are deposited which, when washed with alcohol and dried, are pure hematin.

Hematin is of a reddish colour; its taste is somewhat bitter, and its aqueous solution is yellow when cold, but orange-red at the temperature of boiling water. Sulphuric acid added to this solution renders it reddish yellow. The alkalies give it a purplish tint.

Nicotin.

1820. *Nicotin*. This is a principle existing in tobacco. It was obtained by Vauquelin by the following process:†

Evaporate the expressed juice to one-fourth its bulk; and, when cold, strain it through fine linen; evaporate nearly to dryness; digest the residue in alcohol; filter and evaporate to dryness; dissolve this again in alcohol, and again reduce it to a dry state. Dissolve the residue in water, and saturate the acid which it contains with weak solution of potassa, introduce the whole into a retort, and distil to dryness: re-dissolve, and again distil three or four times successively. The nicotin will thus pass into the receiver, dissolved in water, from which solution it may be obtained by very gradual evaporation.

Nicotin is colourless, acrid, soluble in water and in alcohol, volatile, and highly poisonous.

Asparagin.

1821. *Asparagin*. M. M. Vauquelin and Robiquet obtained this substance in a crystalline form by evaporating the juice of asparagus. It has a cool and slightly nauseous taste, and when burned emits acrid vapours, and leaves no traces of alkali.‡

Bassorin.

1822. *Bassorin* was first noticed by Vauquelin in gum *Bassora*, according to Gehlen and Bucholz, it is contained, together with common gum in the gum tragacanth, and John found it in the gum of the cherry tree. Salop, from the experiments of Caventou, appears to consist almost totally of bassorin.

It is characterized by forming with cold water a bulky jelly which is insoluble in that menstruum, as well as in alcohol and ether. Boiling water does not dissolve it except by long continued ebullition, when the bassorin at length disappears, and is converted into a substance similar to gum arabic. T.

Sarcocoll.

1823. *Sarcocoll* exudes spontaneously from a plant called the *Penea Sarcocolla*. It is generally of a red, or yellow col-

* According to M. Plesson asparagin is identical with a crystalline substance which accompanies the saccharine principle in the liquorice root, and which is called by Robiquet *ageodite*.—*Ann. de Chim.* xxxvii. 81.

† *Ann. de Chim.* lxxii.

‡ *Ann. de Chim.* iv.

our, and is soluble in alcohol and water, forming mucilaginous solutions. Tan causes its immediate precipitation.

1824. *Legumine* is a particular vegetable principle, obtained by M. H. Braconnot from peas. When well washed it resembled paste; exposed to heat it liquefied without coagulating. Iodine, mixed with it in water, appeared to dissolve it. It was insoluble in boiling water, and produced a deep blue colour with starch.* Legumine.

1825. *Inulin*.—The roots of elecampane, when boiled in water, furnish a decoction, which, on cooling, deposits a white powder, in many respects resembling starch. It, however, differs in several properties from that principle, and has hence been considered a peculiar vegetable substance.† Inulin.

1826. *Emetin*.—To obtain emetin, digest powdered ipecacuanha in alcohol, filter, evaporate carefully to dryness, and redissolve in cold water. To this solution add carbonate of baryta, filter, and again evaporate to dryness; digest this residuum in alcohol, and a solution is obtained, which by careful evaporation, affords a reddish-brown substance, soluble in alcohol and in water, and precipitable by sub-acetate of lead; its taste is acrid and bitter, and it is highly emetic.‡ Emetin.

1827. *Woody fibre*.—The term *lignin* has been applied to the fibrous substance which remains, after digesting wood in water and in alcohol. It is insipid, colourless, and insoluble in water. Woody fibre.

1828. We are indebted to M. Braconnot for some highly interesting experiments, relating to the action of sulphuric acid on wood.§ In the course of these researches, he triturated 25 parts of hempen cloth with 34 of the acid; it acquired the consistency of mucilage, which, after 24 hours, was almost entirely soluble in water. The diluted liquor was saturated with chalk, filtered, and evaporated to the consistency of sirup; it deposited sulphate of lime, and was then further evaporated to dryness, when a substance, having the characters of gum, was obtained. In another experiment, 24 parts of lignin were reduced to gum by 34 of sulphuric acid; this acid mixture, diluted with water, and boiled for 10 hours, became sweet; the acid was then separated by chalk, and the liquor, on due evaporation, afforded a crystallizable sugar. Action of sulphuric acid on wood.

Moistened saw-dust, heated in a platinum crucible with its weight of caustic potassa, afforded a matter soluble in water, and which, upon the addition of an acid to neutralize the alkali, yielded a substance having the properties of *ulmin*.

Nitric acid decomposes lignin with the aid of heat, and oxalic, malic and acetic acids are formed.

1829. The woody fibre by exposure to the atmosphere in a perfectly dry state, does not undergo any change. The action Of air.

* *Quart. Jour.* ii. 485.

† Thomson's *System*, vol. iv.

‡ M. M. Magendie and Pelletier, *Annales de Chimie et Physique*, vol. iv.

§ *Ann. de Chim. et Phys.* xii. 172.

of the air upon it, however, when moistened, causes it to pass through various shades of colour, into a black mould. If the process be carried on in a confined portion of oxygen gas, carbonic acid is formed. When excluded from the air, even moist wood shows very little tendency to decomposition.

Composition.

1830. The atomic constitution of lignin, which agrees most nearly with its ultimate analysis is the following :

| | | | |
|------------------|-----------------|------------|-------|
| Carbon | 7 atoms | 42 | 53,86 |
| Oxygen | 4 " | 32 | 41,02 |
| Hydrogen | 4 " | 4 | 5,12 |

78

100. H. 2. 273.

1831. When exposed to heat, lignin affords an acid called the *pyroligneous*, (see *Acetic acid*). By the distillation of wood on a large scale a peculiar spiritous liquid is formed, which was discovered in 1812 by Mr P. Taylor,* and has been examined by M. M. Macaire and Marcet† who proposed for it the name of *pyroxylic spirit*. This liquid is similar to alcohol in many of its properties, but differs from it essentially in not yielding ether by the action of sulphuric acid. It has a strong, pungent, ethereal odour, with a flavour like the oil of peppermint. It boils at 150° F. and its density is 0,828. It burns with a blue flame.

Suber.

1832. *Suber* or *Cork*.—This is a light, soft, elastic, and combustible substance, burning with a bright flame and leaving a bulky charcoal. Its principal peculiarity is, that by digestion in nitric acid, it is converted into an orange-coloured mass, which furnishes to water a peculiar acid matter, which has been termed *suberic acid*. Chevreul has found in it resin, oil, and a peculiar matter which he calls *Cerin*.‡

Cotton.

1833. *Cotton* is a downy substance found in the seed-pods of the different species of *gossypium*. It is insoluble in water and in dilute alkaline and acid solutions. It combines with several of the metallic oxides, which are therefore used as intermedes, or *mordants*, in the art of dyeing. Acetate of alumina is principally employed for this purpose.

Medullin.

1834. *Medullin* is a term given by Dr John to the pith of the sun-flower and some other plants; it is insipid, inodorous, insoluble in water and alcohol, and affords oxalic acid when treated by nitric acid; submitted to destructive distillation, the products abound in ammonia.

1835. *Dracine* is a substance found by M. Melandri in Dragon's blood;§ *Altheine* was obtained by M. Bacon from the *Althea officinalis*.||

* Quart. Jour. xiv. 436.

† Ann. Philos. N. S. viii. 69.

‡ See War.

§ Ann. Philos. N. S. ii. 394.

|| Ibid. 7. 69.

SECTION VII. Tannin.

1836. Tannin, or the astringent principle, is contained in many vegetables. It may be procured by digesting bruised gall-nuts, grape-seeds, oak-bark, or catechu, in a small quantity of cold water. The solution affords, when evaporated, a substance of a brownish-yellow colour, extremely astringent, and soluble in water and in alcohol. Extraction.

The purest form of tannin appears to be that derived from bruised grape-seeds, but even here it is combined with other substances, from which it is perhaps scarcely separable, and among the numerous processes which have been devised for procuring pure tannin, there is none that answers the intended purpose. Mr Brande recommends the following process as that by which he has obtained tannin of the greatest apparent purity. Digest powdered catechu in water at 33° or 34° , filter and boil the solution, which, on cooling, becomes slightly turbid, and is to be filtered again, and evaporated to dryness; cold water, applied as before, extracts nearly pure tannin.*

1837. The most distinctive character of tannin is that of affording an insoluble precipitate when added to a solution of isinglass, or any other animal jelly. Hence infusion of tan is used as a test of the presence of gelatine, and, reciprocally, solution of gelatine may be used as a test of the presence of tan. The solution of gelatine, or jelly, may be prepared for the purpose of precipitating tan, by dissolving isinglass in water, in the proportion of ten grains to two ounces. The precipitate which has been called *Tanno-gelatine* consists of 54 jelly and 46 tan. An excess of the solution partly redissolves it. Properties

Upon this property the art of tanning depends, for which oak-bark is generally employed; the barks, however, of many other trees may occasionally be substituted.† Tanning.

1838. Tan forms a precipitate with solution of starch, with gluten and albumen, and with many of the metallic oxides.‡ Union with other bodies. Metallic oxides.

1839. If the solution of tan, obtained as above-described from catechu, be added to acetate of lead, an insoluble *tannate of lead* falls. From an analysis of this compound, Berzelius states, that 100 parts of tannin are composed of carbon 50,55, oxygen 45, and hydrogen 4,45.

1840. Mr Hatchett has shown that tan may be formed artificially by digesting charcoal in dilute nitric acid during several days; it is at length dissolved, and a reddish brown liquor is obtained, which furnishes, by careful evaporation, a brown Artificial tan.

* For other processes, see Henry, 2 264.

† For a Table exhibiting the average quantity of tan contained in 480 lbs of different barks, see Davy's *Agricultural Chemistry*, 4to. p. 79.

‡ An account of the precipitates formed in metallic solutions by infusion of galls, will be found in the *Tables*: but these precipitates are very complex, and vary in composition.

glossy substance, amounting to about 120 parts from 100 of charcoal.

This *artificial tannin* appears to differ in one circumstance only from natural tannin, which is, that it resists the action of nitric acid, by which all the varieties of natural tannin are decomposed, though some are more capable of resisting its action than others.

Artificial tannin has a bitterish astringent taste, is soluble in water and alcohol, and forms an insoluble precipitate in solutions of animal gelatine, the precipitate consisting, according to Mr Hatchett, of 36 tannin + 64 gelatine.

Action of
acids.

Muriatic and sulphuric acids occasion brown precipitates, in solution of artificial tan, which are soluble in hot water. It combines with the alkalies, and forms a precipitate of difficult solubility in aqueous solutions of lime, baryta, and strontia, and in most metallic solutions; these precipitates are of a brown colour.

1841. A variety of artificial tan is formed by digesting camphor and resins in sulphuric acid till the liquor becomes black, and on being poured into water, deposits a black powder, which, by digestion in alcohol, furnishes a brown matter, soluble in water, and forming an insoluble precipitate with gelatine.*

SECTION VIII. Colouring Matter.

Dyeing.

1842. The colouring matter of vegetables appears to reside in several of their principles, and is therefore very differently acted on by solvents. Its extraction, and transfer to different substances, constitutes the *art of Dyeing*.

1843. Different materials not only possess very different attractions for dye stuffs, but they absorb the colouring matter in very different proportions. Wool appears in this respect to have the strongest attraction for colouring substances: silk comes next to it; then cotton; and, lastly, hemp and flax.

1844. Colours have been divided by Dr Bancroft, in his work on *permanent Colours*, into *substantive* and *adjective*. The former communicate colour without the intervention of any other substance. They have an attraction for the fibre of cloth or linen, and are permanently retained. The latter require the intervention of some body, possessed of a joint attraction for the colouring material and stuff to be dyed. The substance capable of thus fixing the colour, has been called a *basis*, or *mordant*.

Mordants.

1845. The mordants most frequently applied are *acetate of alumina*, *sulphate* or *acetate of iron*, and *muriate of tin*.

* Hatchett's *Phil. Trans.* 1805, 1806.

The substance to be dyed is first impregnated with the mordant, and then passed through a solution of the colouring matter, which is thus fixed in the fibre, and its tint is either modified or exalted by the operation.

The following are the modes of producing some of the principal colours.

1846. *Black* is produced by astringents and salts of iron, and if intended to be deep and perfect, the cloth should previously be dyed blue with indigo. The stuff is first soaked in a bath of galls, then rinsed, and passed repeatedly through a solution of sulphate of iron in infusion of logwood; exposure to air deepens the colour, which at first has a purplish tint. Logwood tends considerably to improve the black, and prevents its acquiring a rusty or brown hue. Sometimes madder is used for the same purpose. Silk is dyed black nearly in the same way, but it requires a much larger relative proportion of galls, and the operation must be frequently repeated. It is difficult to give a good and permanent black to calico; in this process, acetate of iron, galls, and madder are generally used, and the colour is rendered more durable by previously steeping the goods in a weak solution of glue. Black.

Grey is produced by the same operations as black, but the materials are used in a very dilute state. Grey.

1847. *Blue* is chiefly derived from *indigo*, a substance produced by fermenting the leaves of several species of the *indigofera*, a plant abundantly cultivated in South America and in the East Indies. Blue.

1848. *Indigo* is a substance of a deep blue colour, containing about 50 *per cent.* of pure colouring matter, which is perfectly insoluble in water; when heated it sublimes in the form of a blue smoke, which on condensation, forms acicular crystals. It is soluble in concentrated sulphuric acid. This solution is usually called *Saxon* or *liquid blue*, and is used as a substantive colour for dyeing cloth and silk. Substances which powerfully attract oxygen render indigo green, and by exposure to air, it again acquires a blue colour. In this green state indigo is soluble in the alkalies, and the solution is commonly employed for dyeing calico. A bath for this purpose may be made by mixing one part of indigo, two parts of sulphate of iron, and two of lime, in a sufficient quantity of water: in this case the sulphate of iron is decomposed by a portion of the lime. The protoxide of iron thus produced becomes peroxidized at the expense of the indigo, which is rendered green and soluble in the alkaline liquor; cotton steeped in this solution acquires a green colour, which by exposure to air, and washing in water acidulated with sulphuric acid, becomes a permanent blue. Indigo.

A little iron or zinc thrown into diluted sulphate of indigo, changes or destroys the colour in consequence of the evolution of hydrogen; the colour is also quickly impaired and destroyed by chlorine.

Analysis of
indigo.

1849. The analysis of indigo, to ascertain the proportion of colouring matter, which varies much in different samples, may be performed by the successive action of water, alcohol, and muriatic acid.* 100 parts of Guatemala indigo, thus treated, afforded

| | | | | |
|---------------------|---|--|---|------|
| To Water . . | { | Green matter combined with ammonia | } | 12 |
| | | Deoxidized indigo | | |
| | | Extract | | |
| To Alcohol | { | Gum | } | 30 |
| | | Green matter | | |
| | | Resin | | |
| To Muriatic Acid | { | A trace of indigo | } | 6 |
| | | Red resin | | |
| | | Carbonate of lime | | |
| To Muriatic Acid | { | Oxide of Iron | } | 2 |
| | | Alumina | | |
| | | Alumina | | |
| Residue . . | { | Silica | } | 3 |
| | | Pure indigo | | |
| | | Pure indigo | | |
| | | | | 45 |
| | | | | 100† |

Effect of
chlorine.

1850. Chlorine destroys its colour, and the same quantity of free chlorine discolours always the same quantity of indigo. Hence a solution of indigo in sulphuric acid has been employed for measuring the strength of solutions of chlorine and of chloride of calcium, in order to regulate their application to the process of bleaching.‡

To obtain
pure indigo.

1851. To obtain indigo of sufficient purity for experiment, the yellow solution of de-oxidized indigo by lime, which forms the dyer's blue vat, may be agitated in contact with air, which will revive the indigo, and precipitate it purified to a certain degree. The precipitate may be digested in dilute muriatic acid, which will remove a little iron and carbonate of lime. It is then to be washed with distilled water, and dried.§

Indigo may be purified more completely by sublimation. About ten grains of purified indigo, in lumps of about 1 grain, may be placed in a shallow metallic capsule of about 3 inches diameter, covered with a similar capsule, the concave sides of

* Chevreul, *Ann. de Chim.* lxxi. 120.

† In order to find the value of any sample of indigo, Mr Dalton directs to take one grain, carefully weighed from a mass finely pulverized, put this into a wine-glass, and drop two or three grains of concentrated sulphuric acid upon it. Having triturated them well, pour in water, and transfer the coloured liquid into a tall cylindrical jar, about one inch inside diameter. When the mixture is diluted with water, so as to show the flame of a candle through it, mix the liquid solution of chloride of calcium with it, agitating it slowly, and never putting in any more until the smell of the preceding portion has vanished. The liquid soon becomes transparent, and of a beautiful greenish yellow appearance. After the dross has subsided, the clear liquid may be poured off, and a little more water put into the sediment with a few drops of chloride of calcium and a drop of dilute sulphuric acid; if more yellow liquid is produced, it arises from particles of indigo which have escaped the action of the chloride before, and must be added to the rest. The value of the indigo Mr Dalton considers to be in proportion to the quantity of real chloride of calcium necessary to destroy its colour. See *Manchester Memoirs*, N. S. iv. 437.—M. Morin proposes another process, see *Quart. Jour.* N. S. vi. 484.

‡ For a description of an instrument for this purpose contrived by M. Gay-Lussac, see *Ann. de Chim. et Phys.* for June 1824.

§ See an interesting paper, containing "Experiments and Observations on Indigo, and on certain substances which are produced from it by means of Sulphuric Acid," by Mr Walter Crum of Glasgow, in the *Annals of Philosophy*, N. S. v. 81.

both being placed inwards, and at a distance not exceeding three-eighths of an inch in the middle. Mr Crum used two platinum crucible covers, but similarly shaped vessels of other metals would probably answer equally well. The lower capsule is to be heated by a spirit-lamp; and when a hissing noise, which at first attends the process, has nearly ceased, the lamp is to be withdrawn, and the apparatus allowed to cool. On removing the cover, the sublimed indigo is found planted on its inner surface, forming long flat needles, in quantity equal to 18 or 20 per cent. of the original weight, and of a brilliant and intense copper colour. The colour, however, varies with the circumstances under which the crystals are observed. The specific gravity of the sublimate is 1.3.

1852. Sublimed indigo is fusible and volatile at a heat of about 550° Fahrenheit, leaving no residue when heated in open vessels. Its vapour is transparent and of a beautiful violet colour, differing from that of iodine by a shade of red. The melting point of indigo, that at which it sublims, and that at which it is decomposed, appear to be remarkably near each other. Boiling oil of turpentine dissolves enough of purified indigo to acquire the same fine violet colour as its vapour, but deposits it again on cooling.

By the ignition of sublimed indigo with peroxide of copper in green glass tubes, its analysis gave

| | |
|--------------------|--------|
| Carbon | 73,22 |
| Azote | 11,26 |
| Oxygen | 12,60 |
| Hydrogen | 2,92 |
| | <hr/> |
| | 100,00 |

These numbers correspond very nearly to

| | | | |
|------------|------------|---------------|-------|
| Carbon . . | 16 atoms = | 96 . . or . . | 73,84 |
| Azote . . | 1 ditto = | 14 . . or . . | 10,77 |
| Oxygen . . | 2 ditto = | 16 . . or . . | 12,31 |
| Hydrogen . | 4 ditto = | 4 . . or . . | 3,08 |

Equivalent number . . . 130 . . . 100,* H. 2. 280.

1853. By the action of nitric acid upon indigo a substance is obtained in yellow brilliant crystalline plates, which exhibits acid properties, and has been called by Dr Liebig *carbazotic acid*, a name derived from its composition, which is as follows:

| | | | | |
|--------|--------|----|----|-------|
| Carbon | 35,043 | or | 15 | atoms |
| Azote | 16,167 | " | 3 | " |
| Oxygen | 48,790 | " | 15 | " |

1854. To obtain carbazotic acid the following process has been given by Dr Liebig.

A portion of the best indigo is to be broken into small fragments, and moderately heated with 8 or ten times its weight of nitric acid of moderate strength. It will dissolve, evolving nitrous vapours and swelling up in the

* Mr Crum objects, properly to the application of the term *indigogene*, applied by Brugnatelli to sublimed indigo, and denies the power, which has been ascribed to the sublimate, of amalgamating with mercury.

† *Quart. Jour. N. S.* vi. 496.

vessel; after the scum has fallen, the liquid is to be boiled, and nitric acid added as long as any red vapours are disengaged. When the liquid has become cold, a large quantity of semi-transparent yellow crystals will be formed, and if the operation has been well conducted, no artificial tannin or resin will be obtained. The crystals are to be washed with cold water, and then boiled in water sufficient to dissolve them. If any oily drops of tannin form on the surface of the solution, they must be carefully removed by touching them with filtering paper. Then filtering the fluid, and allowing it to cool, yellow brilliant crystalline plates will be obtained, which will not lose their lustre by washing. To obtain the substance perfectly pure, the crystals must be redissolved in boiling water, and neutralized by carbonate of potassa. Upon cooling, a salt of potassa will crystallize, which should be purified by repeated crystallizations.

Properties.

1855. When the substance is heated, it fuses, and is volatilized without decomposition; when subjected to a strong heat, it inflames without explosion, its vapours burning with a yellow flame, and a carbonaceous residue remaining. It is but little soluble in cold water, but much more so in boiling water; the solution has a bright yellow colour, reddens litmus, has an extremely bitter taste, and acts like a strong acid on metallic oxides, dissolving them, and forming peculiar crystallizable salts.—Ether and alcohol dissolve it readily.

Carbazotic acid combines with bases and forms salts called *carbazotates*.*

* *Carbazotate of Potassa* crystallizes in long, yellow, semi-transparent and very brilliant needles; it dissolves in 260 parts of water at 59° F. Strong acids decompose it. When a little is gradually heated in a glass tube, it first fuses, and then suddenly explodes, breaking the tube to atoms; traces of charcoal are observed on the fragments. The slight solubility of this salt supplies an easy method of testing and separating potassa in a fluid. Even the potassa in tincture of litmus may be discovered by it, on the addition of a few drops of carbazotic acid dissolved in alcohol, to infusion of litmus, crystals of the salt gradually separate. The salt contains no water of crystallization. Its composition is potassa 16,21 acid 83,79.

Carbazotate of Soda crystallizes in fine silky yellow needles, having the general properties of the salt of potassa, but soluble in from 20 to 24 parts of water, at 59° F.

Carbazotate of Ammonia, forms very long, flattened, brilliant, yellow crystals, very soluble in water. Heated carefully in a glass tube, it fuses, and is volatilized without decomposition; heated suddenly, it inflames without explosion, and leaves much carbonaceous residue.

Carbazotate of Baryta, obtained by heating carbonate of baryta, and carbazotic acid with water, crystallizes in quadrangular prisms of a deep colour, and dissolves easily in water. When heated it fuses, and is decomposed with very powerful explosion, producing a vivid yellow flame: 100 parts lose at 212° F. 125 parts of water: 100 parts of the anhydrous salt contain 75,72 acid, and 24,28 baryta.

Carbazotate of Lime, obtained like the salt of baryta, forms flattened quadrangular prisms, very soluble in water, and detonating like the salt of potassa.

Carbazotate of Magnesia forms very long indistinct needles, of a clear yellow colour, is very soluble, and detonates violently.

Carbazotate of Copper, prepared by decomposing sulphate of copper by carbazotate of baryta: it crystallizes with difficulty, the crystals being of a fine green colour; it is deliquescent; when heated it is decomposed without explosion.

Carbazotate of Silver. Carbazotic acid readily dissolves oxide of silver, when heated with it and water; and the solution, gradually evaporated, yields starry groups of fine acicular crystals of the colour and lustre of gold; the salt dissolves readily in water: when heated to a certain degree, it does not detonate, but fuses like gunpowder.

Proto-carbazotate of Mercury, obtained in small yellow triangular crystals, by mixing boiling solutions of the carbazotate of potassa or soda, and proto-nitrate of mercury. It requires more than 1200 parts of water for its solution: it consists of 53,79 acid, and 46,21 protoxide of mercury per cent.

Carbazotate of Lead may be formed by decomposing a salt of lead by carbazotate of potassa or soda; it is a yellow powder, but slightly soluble, and detonating by heat.

All these salts detonate much more powerfully when heated in close vessels, than when heated in the air, and what is remarkable, those with bases yielding oxygen most readily are those which explode with least force.—*Ann. de Chim.* xxv. 72; and *Quart. Jour. N. S.* iii.

1856. By the action of sulphuric acid on indigo two new substances are obtained termed by Mr Crum *Cerulin* and *Phenicin*. To prepare the former, the indigo is digested in the acid, the mixture is dissolved in a large quantity of sulphuric acid, and the filtered solution is precipitated by potassa. The precipitate consists of *cerulin*, in combination with the sulphate of potassa, and has been called *Ceruleo-sulphate of potassa*. It requires about 140 parts of water for its solution, and forms a very deep blue coloured liquid. In its property of forming insoluble compounds with neutral salts, cerulin is analogous to tan. From its ultimate analysis it appears to consist of 1 atom of indigo + 4 atoms of water.

Cerulin and Phenicin.

1857. *Phenicin* is procured by stopping the action of the acid on indigo before it is converted into cerulin; diluting, filtering and washing the mixture with water, when it becomes of a bottle green colour: muriate of potassa is added to the blue washings which are finally obtained, when the phenicin is precipitated of a fine reddish purple colour. It is soluble in water, and in alcohol, forming blue-coloured solutions, and is easily converted into cerulin by the action of water. From its ultimate analysis Mr Crum is disposed to consider phenicin as constituted of 1 indigo + 2 water.

Phenicin how procured.

1858. The colouring matter of vegetables, besides being capable of fixation on cloth, may be obtained in a dry form, in combination with a base only. Thus, if to a decoction or infusion of madder in water, a solution of sulphate of alumina be added, the colouring matter is precipitated in combination with the alumina, forming what is termed a *lake*. For obtaining this, the following process is given by Sir H. Englefield.

Lakes,

Put two ounces of Dutch crop-madder into a calico bag, capable of holding three or four times that quantity. Pour on it a pint of distilled water, and triturate, in a mortar, as much as can be done, without destroying the bag. The water becomes loaded with colouring matter, and is opaque and muddy. Pour off this portion, and repeat the operation till no more colour is obtained, which will generally happen after the fifth or sixth affusion. Pour these several washings into an earthen or well tinned copper pan; and apply heat till the liquor boils. Let it then be poured into a basin; and one ounce of alum, dissolved in a pint of water, be added, and mixed by stirring. Add an ounce and a half of saturated solution of sub-carbonate of potassa; a violent effervescence will ensue, and the colouring matter will be precipitated. Stir the mixture till cold, and wash repeatedly with boiling water. About half an ounce of lake will be obtained, containing two-fifths its weight of alumina.

Other lakes may be obtained of different colours, by the substitution of different dyeing-woods; and from the infusion of cochineal, the beautiful pigment called Carmine is precipitated by means of a solution of tin. H: 2, 283.

1859. *Yellow*.—There are several dyestuffs employed in the production of yellows. A decoction of *Weld* (*Reseda Luteola*), with an aluminous mordant gives a good yellow, which is rendered more brilliant by tartar, and by permuriate of tin.

Yellow.

The bark of the American oak (*Quercus Nigra*), or *Quercitron bark*, also furnishes excellent yellows; it was first intro-

duced into England by Dr Bancroft, who has fully and philosophically detailed its various applications.* The salts of alumina and of tin are the principal mordants employed both with wool and cotton.

Fustic wood, *sumac*, and *dyers' broom*, are also occasionally employed as sources of yellow colours.

Reds.

1860. *Reds* are chiefly produced from *madder*, the prepared root of the *Rubia Tinctorum*. The colouring matter is fixed by an aluminous mordant, assisted by galls, but the process is very complex and circuitous. In Dr Bancroft's work above quoted (vol. ii.) are full details upon this subject; and a per-spicious abstract of them will be found in AIKIN'S *Dictionary*, Art. *Dyeing*.

Brazil wood, *safflower*, and *logwood* are occasionally employed as red or pink dyestuffs, but they only give fugitive colours.

Scarlet.

1861. *Scarlet* is produced exclusively with the colouring matter of the *cochineal*, a small insect brought from Mexico, where it is found upon different species of the *Opuntia*. The nature of this colouring matter has been investigated by M. M. Pelletier and Caventou; it is united in the insect with a peculiar animal matter, fat, and some saline substances; they separated it by exposing a strong alcoholic tincture of cochineal to spontaneous evaporation; it deposited a crystalline matter, which was re-dissolved in alcohol and the solution mixed with its bulk of sulphuric ether; this caused it in a few days to deposit the pure colouring principle, which they call *Carminium*: Dr John has proposed for it the term *Coccinellin*. This substance is fusible at about 120°, very soluble in water, less so in alcohol, and insoluble in ether; the acids change its colour from purple to pale red or yellow: the alkalis render it violet; and its colour is impaired by most saline solutions. It readily combines with alumina, forming a beautiful *lake* or *carmine*.

Carmine.

The colouring matter of cochineal is fixed upon wool by nitromuriate of tin and tartar, by which scarlets are produced and alum changes the scarlet to crimson. Cotton and linen are very rarely dyed with cochineal, for independent of its great expense, the colours are little superior to those given by madder.

Buff.

1862. *Buff* and *Fawn Colour* are produced in a variety of ways. *Walnut-husks* and *Sumac*, with alum mordants, give durable colours of this description, which are rendered *Drab*, or *Grey*, by a very little iron.

Green.

1863. *Green* is obtained on woollen cloth, by passing it through the green indigo vat, and then dyeing it as for simple yellows, the relative proportion of the blue and yellow being adjusted to the intended intensity of the green. Silk is first dyed yellow, and afterwards blued with indigo. *Saxon green* is done by dyeing yellow upon a Saxon blue ground. A solu-

* Experimental Researches concerning the Philosophy of Permanent Colours, &c. London, 1813.

tion of verdigris in vinegar is sometimes used to produce a delicate green; pearlash is added before it is used, and the cotton previously impregnated with the alum mordant, is then passed through the mixture.*

1864. *Calico-printing* is a more refined and difficult branch of the art of dyeing. In this process adjective colours are almost always employed. The mordants, the principal of which are acetate of alumina, and acetate of iron, are first applied to the calico by means of wooden blocks or copper plates, upon which the requisite patterns are engraved. The stuff is then passed through the colouring bath, and afterwards exposed on the bleaching ground, or washed. The colour flies from those parts which have not received the mordant, and is permanently retained on those parts only to which the basis has been applied: variety of colours is produced by employing various mordants and different colouring materials. Calico printing.

White spots upon a dark ground are sometimes produced by covering the parts with wax, pipe-clay, or other materials, which prevent the contact of the colour; or citric acid, thickened with gum, is applied, like a mordant with a block or plate which prevents the retention of the colour. Sometimes the colour is discharged in places by the application of chlorine.†

SECTION IX. Wax.

1865. This principle exists in many plants; it may be obtained by bruising and boiling them in water; the wax separates and concretes on cooling.

The berries of the *Myrica cerifera*, and the leaves and stem of the *Ceroxylon* afford considerable quantities of wax by this process.‡ The glossy varnish upon the upper surface of the leaves of many trees is of a similar nature, and though there are shades of difference, these varieties of wax possess the essential properties of that formed by the bee.

1866. Pure wax is colourless and insipid; its specific gravity Propriétés. is about .96: it is insoluble in water, and fusible at a temperature of about 150°; at a higher temperature it is converted into vapour, and at a red heat it burns in the contact of air with a bright flame. It is sparingly soluble in boiling alcohol and ether, and is deposited as the solutions cool. The fixed oils, when assisted by heat, readily dissolve it, and form a compound

* Besides the above, an infinite variety of compound colours are formed, by mixtures of the simpler tints, and of the mordants; for practical details see Dr Bancroft's *Treatise*, and Berthollet on *Dyeing*.

Zanthopierite.—M. M. Chevalier and Pelletan have given this name to a crystallized colouring substance which they have extracted from the bark of the *Zanthoxylum* of the Carribee Islands.—See *Ann. Philos. N. S.* ii. 69.

† See Parkes' *Essays*, v. 1. and *Boston Jour. of Philos.* iii.

‡ Bostock, *Nicholson's Journal*, vol. iv. Brande, *Phil. Trans.* 1811. Dana, in *American Journal of Science*, i.

Cerates.

of variable consistency, which is the basis of *cerates* and *ointments*. Some of the volatile oils also dissolve wax, when aided by heat. It is soluble in the fixed alkalis, forming soapy compounds; but the acids scarcely act upon it; hence the advantage of *wax-lute* for the retention of corrosive vapours.

Cerin.

Myricin.

1867. When bees'-wax, or myrtle-wax, are digested in boiling alcohol, they afford, according to Dr John, a soluble and insoluble portion; he has called the former *cerin*, the latter *myricin*. Cerin is insoluble in water and in cold alcohol and ether, but dissolves in those liquids when heated. Myricin is insoluble, under all circumstances, in alcohol and ether.

Cérine.

The term *cerine* has been applied by Chevreul to a principle resembling wax which he separated from cork; it is less fusible than wax, more soluble in alcohol, and partly converted into oxalic acid, by the action of nitric acid.

Analysis of
wax.

1868. Gay-Lussac and Thenard, and Dr Ure, have analyzed yellow wax by combustion with peroxide of copper and deduced its elements to be

| | | |
|--------------------|------------------|-------|
| Carbon | 81,784 | 80,69 |
| Oxygen | 5,544 | 7,94 |
| Hydrogen | 12,672 | 11,37 |
| | 100,* | 100,† |

The atomic constitution, most consistent with these results is,

| | | | |
|--------------------|--------------------|--------------|-------|
| Carbon | 13 atoms | 78 | 80,41 |
| Oxygen | 1 atom | 8 | 8,26 |
| Hydrogen | 11 atoms | 11 | 11,33 |
| | | 97 | 100. |

But it is not improbable, as Dr Ure has remarked, that an atom more of hydrogen may exist in wax than has been discovered by analysis, and that it may consist of 12 atoms of olefiant gas + 1 atom of carbonic oxide. H. 2. 294.

SECTION X. Fixed Oil.

1869. Fixed Oil is generally obtained by pressure from certain seeds, such as the almond, linseed, and many others and from the olive.† The specific gravity of the fixed oils, is usually a little below that of water. They are viscid; insipid, or nearly so; and generally congeal at a temperature not so low as that required to freeze water. A few of them are solid at the ordinary temperature, and have been called *vegetable butters*. They are insoluble in water, but by the aid of mucilage may be diffused through it, forming *emulsions*. They are for the

Emulsions.

* *Recherches*, iii.

† *Phil. Trans.* 1822.

‡ Olive oil is sometimes adulterated with that of certain seeds, which may be detected by the action of nitrate of mercury. For this purpose, 6 parts of mercury are dissolved without heat, in 7,5 parts of nitric acid, specific gravity 1,36; this solution, shaken with olive oil, becomes solid in a few hours; but if sophisticated with oil of grains, it does not solidify it.

most part sparingly soluble in alcohol and ether, though castor-oil dissolves in any quantity in those fluids.*

1870. Fixed oils and fats are not pure proximate principles, but consist of two substances, one of which is solid at common temperatures, while the other is fluid. To the former Chevreul has applied the name of *Stearine* from *στέαρ* suet, and to the latter *Eläine* from *ελαίον* oil. Stearine is the chief ingredient of suet, butter, and lard, and is the cause of their solidity; whereas oils contain a greater proportional quantity of eläine, and are consequently fluid. These principles may be separated from one another by exposing fixed oil to a low temperature, and pressing it when congealed, between folds of bibulous paper. The stearine is thus obtained in a separate form; and by pressing the bibulous paper under water, an oily matter is procured which is eläine in a state of purity.†

Stearine and eläine.

M. Pictet's method of procuring eläine, consists in pouring upon oil a concentrated solution of caustic soda, stirring the mixture, heating it slightly to separate the eläine from the soap of the stearine, pouring it on a cloth, and then separating by decantation the eläine from the excess of alkaline solution.

1871. When the gum of olive oil is dissolved in alcohol, and the solution is allowed to evaporate spontaneously, a peculiar substance is deposited in flattened needles, or as a brilliant amylaceous powder, to which M. Pelletier, its discoverer, has given the name of *olivile*.‡

Olivile.

1872. These oils cannot be volatilized without decomposition, which takes place at a temperature of about 600°, and water is copiously formed, attended by the separation of carbonaceous matter, which causes the oil to blacken and grow thick; a portion of acetic acid is also at the same time formed. If the vapour be collected, it is found acrid, sour, and empyreumatic; it was formerly employed in pharmacy, under the name of *philosopher's oil*, and as it was often obtained by steeping a brick in oil, and submitting it to distillation, it was also called *oil of bricks*. Passed through a red hot tube, the fixed oils furnish a very large proportion of carburetted hydrogen gas; and when burned in the wicks of lamps they suffer a similar decomposition, and water and carbonic acid are the products of their combustion.

Oil of bricks.

1873. The greater number of the fixed oils undergo little other change by exposure to air than that of becoming some-

* Brando, *Phil. Transactions*, 1811.

† For the purpose of lubricating delicate wheel-work, as in chronometers, clocks, &c. it is important that oil should be free from every kind of acid, or of mucilage, that it should in fact be pure eläine, without any trace of stearine. In order to extract the eläine from fixed oils M. Chevreul treats it in a matrass, with 7 or 8 times its weight of alcohol nearly boiling, decanting the liquid, and exposing it to cold. The stearine will then separate in the form of a crystallized precipitate. The alcoholic solution must then be evaporated to the fifth of its volume, and the remainder will be eläine, which ought to be colourless, insipid, almost without smell, without any action on the infusion of tursole, having the consistence of white olive oil, and coagulable with difficulty. *Edin. Jour.*

‡ *Ann. Philos.* xii.

what more viscid, and acquiring a degree of rancidity. In this state they contain free acid, and redden vegetable blues. Some few such as linseed, and nut-oil, and the oils of the poppy and hemp-seed become covered with a pellicle, and when thinly spread upon a surface, instead of remaining greasy, become hard and resinous; these are termed *drying oils*, and their drying quality is much improved by boiling them upon a small quantity of litharge.

Drying oil.

1874. The drying oils, and especially nut-oil, form the basis of *printer's ink*, the history of which will be found in LEWIS'S *Phil. Commerce of the Arts*. The oil is heated and set fire to, and after having been suffered to burn for half an hour is extinguished, and boiled till it acquires a due consistency; in this state it is called *Varnish*, and is viscid, tenacious, and easily miscible with fresh oil, or with oil of turpentine, by which it is properly thinned, and afterwards mixed with about one-eighth part of lamp-black.

Printers' ink.

Action of
nitric acid.

1875. Nitric acid acts with great energy on the fixed oils. In a small proportion, its chief effect is to render them thicker. When distilled together with a large proportion of acid, the oil is decomposed, and nitrous gas disengaged; oxalic acid remaining in the retort. Red and smoking nitric acid, when suddenly mixed with a fixed oil, especially with the addition of a little sulphuric acid, occasions a violent combustion. Chlorine gas, passed through them, thickens them, and renders them tenacious like wax. H.

Action of
alkalies.

Soap.

1876. The alkalies readily combine with the fixed oils, and form white compounds called *Soap*. Of these the most important is the *soap of soda*, which is thus made: Five parts of barilla are mixed with one of lime and a proper quantity of water. In this way a *ley*, or solution of caustic soda, is obtained, which is boiled in an iron pot with six parts of oil till the soap separates, which is accelerated by the addition of common salt; it is then suffered more perfectly to congeal, and in a few days becomes hard enough to cut into forms.* The best soaps are made with olive oil and soda; in this country animal fat is usually employed for the common soaps, to which resin and some other substances are occasionally added. *Soft Soap* is a compound of potassa with some of the common oils; even fish oil is often used.

1877. In the formation of soap the stearine and eläine, according to Chevreul, disappear entirely, being converted by a change in the arrangement of their elements into three compounds, to which he has applied the names of *margaric* and *oleic* acids, and *glycerine*. The two acids enter into combination with the alkali employed, and the resulting compound is soap.

Transparent
soap.

1878. Soap furnishes a milky solution with water. It dissolves in alcohol, and the solution, if concentrated, is of a

* Ajkin's Dictionary, Art. Soap.

gelatinous consistency. By carefully distilling off the alcohol, a transparent soap is obtained.

The acids and the greater number of salts decompose soap, forming in most cases a compound of difficult solubility ; hence hard waters are unfit for washing, in consequence of containing sulphate of lime ; hence also the alcoholic solution of soap is usual as a test for ascertaining the fitness of water for this purpose, which, if it becomes very turbid, cannot in general be used for washing.

When soaps are decomposed by the acids, the oil which they contain is found to have undergone a change, the history of which will be noticed under the head of animal oils.

1879. The fixed oils readily combine with oxide of lead, when aided by heat, forming the compound usually termed plaster ; with the oxides of mercury and bismuth they produce very similar combinations, and are also capable of dissolving white arsenic in large proportion.

1880. The ultimate components of olive oil, as given by Gay-Lussac and Thenard, are

| | | |
|--------------------|--------|-----------|
| Carbon | 77,213 | Analysis. |
| Oxygen | 9,427 | |
| Hydrogen | 13,360 | |
| | 100. | |

From these proportions it is inferred that olive oil probably consists of

10 atoms of carbon, 1 atom of oxygen, 11 atoms of hydrogen.

1881. The fixed oils have a singular property, which has led sometimes to serious accidents. When mixed with lampblack, or with any light kind of charcoal, and even with several vegetable substances, as cotton, wool, or flax, the mixture, after some time, heats spontaneously, and at length bursts into flame. This combustion has sometimes been observed to take place in the waste cotton, employed to wipe the oil from machinery ; and has probably occasioned many of the dreadful fires, which have happened in cotton-mills, and for which no adequate cause could be assigned.*

SECTION XI. Volatile Oils.

1882. These oils are generally obtained by distilling the plants which afford them with water in common stills ; the water and oil pass over together, and are collected in the Italian recipient shown in fig. 125, in which the water having reached the level a b, runs off by the pipe c, and the oil being generally lighter than water, floats upon its surface in the space d. The whole contents of the recipient are then poured into a funnel,

* See Quart. Jour. v. 367.

the tube of which is closed with the finger, and when the oil has collected upon the surface, the water is suffered to run from it, and the oil transferred into a bottle. The distilled water being saturated with the oil, should be retained for a repetition of the distillation. The produce of oil is sometimes increased by adding salt to the water in the still, so as to elevate its boiling point a few degrees.

Some of the volatile oils are obtained by expression, such as those of *lemon*, *orange*, and *Bergamot*, which are contained in distinct vesicles in the rind of those fruits.

1883. The volatile oils vary considerably in specific gravity, as will be seen by referring to the *Tables*.

Properties.

The volatile oils have a penetrating odour and taste, and are generally of a yellowish colour; they are for the most part very soluble in alcohol, and very sparingly soluble in water; these solutions constitute *perfumed essences* and *distilled waters*. The latter are principally employed in pharmacy, and the former as perfumes.

When pure they pass into vapour at a temperature somewhat below that of 212° , when distilled with water, they pass over at its boiling point. They are inflammable, and water and carbonic acid are the results of their perfect combustion. As many of these oils bear a very high price, they are not unfrequently adulterated with alcohol and fixed oils. The former addition is rendered evident by the action of water; the latter by the greasy spot which they leave on paper, and which does not evaporate when gently heated.

Adulteration.

1884. Nitric and sulphuric acids rapidly decompose the volatile oils.

Exp.

A mixture of four parts of nitric, and one of sulphuric acid, poured into a small quantity of oil of turpentine, produces instant inflammation.

The relative quantity of essential oils, furnished from different materials, is liable to much variation; the products of 1 cwt. of the different vegetable substances are given below.*

Action of air.

1885. Many of the essential oils become changed by exposure to air, and an acid is formed in them, which crystallizing in acicular needles, may be separated. Oil of cassia has been found by M. Bizio, to afford the largest quantity. This acid has neither odour nor taste, is heavier than water, fuses and sublimes by heat, and condenses in brilliant crystals. It burns

| | | Ounces. |
|---------------------------------------|-------------------|-------------------|
| * Juniper berries (common) | - - - - - | 4 to 5 |
| Ditto. (fine Italian) | - - - - - | 7 to 8 |
| Aniseed (common) | - - - - - | 32 to 36 |
| Ditto. (finest) | - - - - - | 36 to 38 |
| | | lbs. oz. lbs. oz. |
| Caraways | - - - - - from 3 | 12 to 4 12 |
| Dill-seed | - - - - - from 2 | to 2 6 |
| Cloves | - - - - - from 18 | to 20 |
| Pimento | - - - - - from 2 | to 3 4 |
| Fennel-seed | - - - - - | 2 |
| Leaves of the <i>Juniperus Sabina</i> | - - - - - | 14 |

in the air with flame, is sparingly soluble in cold water, more readily in boiling water, the acid crystallizing as the water cools. It dissolves in alcohol both at common and high temperatures. Hot nitric acid acts powerfully on it, evolving much nitric oxide, and the substance, which separates when the solution is cold, no longer has the properties of the original acid. Sulphuric acid acts still more powerfully.

1886. If the essential oils be exposed for a longer time to the air, there occurs, at a later period than that of the formation of the acid above described, another change, resulting in the production of a resinous substance, and of strong acetic acid.

1887. Upon subjecting the essential oils to a very low temperature, crystals form in them, and ultimately a separation of them into two parts analagous to the separation of fixed oils into stearine and elaine. M. Bizio has called the most fluid part *Igrusina*, and the solid part *Serusina*.

1888. *Igrusina* is fluid at the lowest artificial temperature ; *Igrusina*, it dissolves in alcohol, and wholly evaporates when heated. When gradually changed by the action of oxygen, it becomes denser, and ultimately is changed into resin and acetic acid.

1889. *Serusina*, obtained from the oil of roses and anise, *Serusina*, is solid at 60° F. ; that from the oils of mint, orange, lemon, &c. required a temperature as low as 4° F. for solidity. It crystallizes in prismatic needles, and sometimes in plates. It is soluble in alcohol.*

SECTION XII. Camphor.

1890. THIS substance in many respects resembles the essential oils ; like them it is volatile, inflammable, soluble in alcohol, and sparingly soluble in water. Soluble in alcohol.

In its ordinary state it is white, semi-transparent, and concrete. Its specific gravity ,98. It fuses at about 300°, in close vessels. It dissolves in the fixed and volatile oils. It is scarcely acted upon by the alkalis ; some of the acids dissolve, others decompose it.† Specific gravity.
Action of oils.

If mixed with bole or powdered clay, and repeatedly distilled, it is almost entirely converted into a liquid, having the characters of essential oil.

The camphor of commerce is obtained from the *Laurus Camphora*, and comes chiefly from Japan. It is originally separated by distillation, and subsequently purified in Europe in a subliming vessel somewhat of the shape of a turnip, from which the cakes of camphor derive their form. Extraction.

* *Giornale de Fisica* ix: 360.—*Quart. Jour.* N. S. ii. 486.

† Hatchett, *Phil. Trans.* 1805. Chevreul, *Ann. de Chim.* lxxiii.

Action of ni-
tric acid.
Camphoric
acid.

1891. When camphor is repeatedly distilled with nitric acid it is converted into *camphoric acid*.

For this purpose four ounces of camphor, reduced to powder by trituring it with a few drops of spirit of wine, may be introduced into a two-quart tubulated retort, placed in a sand-heat: pour upon it 30 ounces of common nitric acid, and proceed to slow distillation. When two thirds of the acid have passed over, return it into the retort and distill as before, repeating the operation twice more; after which, as the liquor cools, a quantity of crystals of camphoric acid are deposited, which are to be washed and dried.

This acid assumes the form of plumose crystals, soluble in about 100 parts of water at 60°, and in rather more than one part of alcohol. Its taste is acid, and somewhat acrid, and it has an aromatic odour. Exposed to heat it sublimes unaltered. It combines with the salifiable bases, constituting a class of salts called *Camphorates*.

Analysis.

1892. The ultimate analysis of camphor has been performed by Dr Ure, who represents its constitution as follows:

| | | | |
|----------------|------------------|------------|-------|
| Carbon | 10 atoms | 60 | 78,02 |
| Oxygen | 1 atom | 8 | 10,40 |
| Hydrogen . . . | 9 atoms | 9 | 11,58 |
| | | 77 | 100 |

Artificial
camphor.

1893. When a current of muriatic acid gas is passed through oil of turpentine,* it deposits a concrete substance, which has been called *artificial camphor*, and the weight of which amounts to about one-half of the oil employed. When purified by sublimation with a little quick-lime, it is rendered pure and white. It is lighter than water, sublimes without decomposition, burns like camphor, and in smell resembles a mixture of camphor and turpentine.† By the action of zinc it affords chloride of zinc, and the oil is evolved little altered.

Action of sul-
phuric acid.

1894. Camphor dissolves in sulphuric acid, forming a brown solution, from which it is at first precipitated, unaltered, by water. Sulphurous acid is afterwards evolved, the solution becomes black and thick, and, after some days, affords a brown coagulum on the addition of water, and smells fragrant and peculiar. On distilling the diluted liquor, water and a yellow oil pass over, a little sulphurous acid is then disengaged, and a black matter remains in the retort, which, when digested in alcohol, affords a portion of soluble matter having some of the properties of artificial tannin.‡

SECTION XIII. Resins.

1895. RESINS are substances which exude from many trees, either from natural fissures or artificial wounds. Common resin

* Thenard is of opinion that no decomposition of the oil of turpentine takes place; but that the muriatic acid unites to it entire. Ordinary camphor, he supposes from analogy, to be a compound of an essential oil and a vegetable acid.

† Thenard, *Memoires d'Arcueil*, (Tom ii.) ‡ Hatchett, *Phil. Trans.*

is obtained by distilling the exudation of different species of fir; *oil of turpentine* passes over, and the resin remains behind. It may be taken as a perfect example of resin, and is possessed of the following properties: It is solid, brittle, a little heavier than water, and acquires negative electricity when rubbed. It has scarcely any taste or smell; is insoluble in water; readily soluble in alcohol, which takes up about one-third its weight, and becomes milky upon the addition of water. Resin is soluble in the caustic alkalies, the solution is saponaceous; and when mixed with an acid, the resin separates, scarcely altered in its properties. Nitric, muriatic, and acetic acids dissolve it without much change.*

1896. A few of the resins derive odour from containing essential oil; some afford benzoic acid when heated, and these have been termed *balsams*; *copal*, *mastich*, and a few others, are very difficultly soluble in alcohol, and contain a substance somewhat analogous to caoutchouc. *Guaiacum* is characterized by the singular changes of colour, which its alcoholic solution suffers when exposed to the action of nitric acid.†

Guaiacum is also rendered blue by the gluten of wheat, but its colour, is not changed by starch; the intensity of the blue colour is said to be proportional to the quantity of gluten present in flour.‡

1897. There is a remarkable want of agreement between different statements of the composition of the same kind of resin, arising, probably, from actual differences of the substance itself. Dr. Ure states the following as the results of his analysis.

| | | | | | |
|----------------|-------|---|---------|---------|----------------|
| Carbon | 75,00 | = | 8 atoms | | 48 |
| Oxygen | 12,50 | = | 1 do. | | 8 |
| Hydrogen . . . | 12,50 | = | 8 do. | | 3 |
| | 100 | | | | 64 H. 2. 253,6 |

1898. *Lac* is a substance formed by an insect, and deposited on different species of trees chiefly in the East Indies. The various kinds of lac distinguished in commerce, are *stick lac*, which is the substance in its natural state, investing the small twigs of the tree: *seed-lac*, which is the same broken off; and which, when melted, is called *shell-lac*. These substances have been examined by Mr Hatchett. Their component parts are exhibited below.—*Phil. Trans.* 1804.||

* The properties of the resins have been very ably investigated by Mr Hatchett, the details of whose researches will be found in his communications to the Royal Society, printed in the *Philosophical Transactions* for 1804, 1805, 1806.

† *Phil. Trans.* 1811.

‡ Taddei, *Giornale de Fisica*, i. 168. *Quarterly Journal*, viii. 376.

§ For other results, see Henry ii. 253.

| | Stick-Lac. | Seed-Lac. | Shell-Lac. |
|--------------------|------------|-----------|------------|
| Resins | 68 | 88,5 | 90,9 |
| Colouring matter . | 10 | 2,5 | 0,5 |
| Wax | 6 | 4,5 | 4,0 |
| Gluten | 5,5 | 2,0 | 2,8 |
| Foreign bodies . . | 6,5 | | |
| Loss | 4,0 | 2,5 | 1,8 |
| | 100 | 100 | 100 |

fords an insoluble precipitate, composed of succinate of iron, of a reddish brown colour. It has been proposed as a means of separating iron in analysis, but is quite inapplicable in the greater number of cases, B.

1905. The resins are applied to a variety of useful purposes ; Uses.
and dissolved in alcohol and oils they constitute the different *varnishes*. The most solid resins yield the most durable var- Varnishes.
nishes.

SECTION XIV. *Vegetable Alkalies.*

1906. Under this title are comprehended those proximate vegetable principles, which are possessed of alkaline properties. The existence of this class of bodies was discovered by Sertuerner, a German apothecary, who published an account of morphia in the year 1803.

1907. All the vegetable alkalies, according to the reseaches Composition.
of Pelletier and Dumas, consist of carbon, hydrogen, oxygen and nitrogen.*

They are decomposed with facility by nitric acid and by heat, and ammonia is always one of the products of the destructive distillation. They never exist in an insulated state in the plants which contain them ; but are apparently in every case combined with an acid, with which they form a salt more or less soluble in water. These alkalies are, for the most part, very insoluble in water, and of sparing solubility in cold alcohol ; but they are all readily dissolved by that fluid at a boiling temperature, being deposited from the solution, commonly in the form of crystals, on cooling. Most of the salts are far more soluble in water than the alkalies themselves, and several of them are remarkable for their solubility. General properties.

1908. As the vegetable alkalies agree in several of their leading chemical properties, the mode of preparing one of them admits of being applied with slight variation to all. The general outline of the method is as follows.—The substance containing the alkaline principle is digested, or more commonly macerated, in a large quantity of water, which dissolves the salt, the base of which is the vegetable alkali. On adding some more powerful salifiable base, such as potassa or ammonia, or boiling the solution for a few minutes with lime or pure magnesia, the vegetable alkali is separated from its acid, and being in that state insoluble in water, may be collected on a filter and washed. As thus procured, however, it is impure, retaining some of the other principles, such as the oleaginous, resinous, or colouring matters with which it is associated in the plant. To purify it from these substances, it should be mixed with a little animal Method of obtaining them.

* *Ann de Chim, et de Phys.* xxiv.

charcoal, and dissolved in boiling alcohol. The alcoholic solution, which is to be filtered while hot, yields the pure alkali, either on cooling or by evaporation, and if not quite colourless, it should again be subjected to the action of alcohol and animal charcoal. In order to avoid the necessity of employing a large quantity of alcohol, the following modification of the process may be adopted. The vegetable alkali, after being precipitated and collected on a filter, is made to unite with some acid, such as the acetic, sulphuric, or muriatic, and the solution is boiled with animal charcoal until the colouring matter is removed. The alkali is then precipitated by ammonia or some other salifiable base. T. 542.

Morphia.

1909. *Morphia*.—Opium contains several of the vegetable principles that have already been enumerated and a peculiar one in which the narcotic virtue resides, called morphia. One of the best processes for preparing pure morphia is that recommended by M. Robiquet.*

The concentrated infusion of a pound of opium is boiled for a quarter of an hour with about 150 grains of pure magnesia, and the greyish crystalline precipitate, which consists of the meconiate of magnesia, morphia, narcotine, colouring matter, and the excess of magnesia, is collected on a filter and edulcorated with cold water. This powder is then digested at a temperature of 120° or 130° F. in dilute alcohol, which removes the narcotine and the greater part of the colouring matter. The morphia is then taken up by concentrated boiling alcohol, and is deposited in crystals on cooling.—By this process half a pound of very pure opium affords three drachms and a half of morphia.

Dr Thomson proposes to precipitate the morphia by ammonia, and to purify it by solution in acetic acid and digestion with animal charcoal.† The animal charcoal should be deprived of phosphate of lime by muriatic acid before being used.‡

Properties.

1910. Pure morphia is white, and crystallizes readily in small rectangular prisms of a brilliant lustre. It is almost wholly insoluble in cold, and to a very small extent in hot water. It is soluble in strong alcohol, especially by the aid of heat. In its pure state it has scarcely any taste; but when rendered soluble by combining with an acid, or by solution in alcohol, it is intensely bitter. It has an alkaline reaction, and combines with acid, forming neutral salts, which are far more soluble in water than morphia itself, and for the most part are capable of crystallizing.

Action of nitric acid.

1911. Strong nitric acid decomposes morphia, forming a red solution, which by the continued action of the acid acquires a yellow colour, and is ultimately converted into oxalic acid.

Action on the system.

1912. When pure, morphia owing to its insolubility, is almost inert; in a state of solution, on the contrary, it acts on the animal system with great energy, Sertuerner having noticed alarming symptoms from so small a quantity as half a grain. From this it appears to follow, that the effects of an over dose of a salt of morphia may be prevented by giving a dilute solution of ammo-

* *Ann. de Chim. et de Phys.* v.† *Ann. Philos.* xv.‡ For a method of extracting morphia from dry poppy heads see *Quart. Jour.* N. S. iii. 216.

nia, or an alkaline carbonate, so as to precipitate the vegetable alkali.

1913. When carefully administered, morphia may be employed very advantageously in the practice of medicine, since, according to Magendie, it produces the soothing effects of opium, without causing the feverish excitement, heat and headach, which so frequently accompany the employment of that drug. The best mode of exhibiting it, is in the form of the acetate of morphia, a salt which is very soluble in water, and crystallizes in divergent prisms by evaporation.*

1914. The composition of morphia has been stated differently by different chemists, as will appear from the following numbers.

| | | | | | | | | | |
|----------|-------|-------|-------|-------|-------|-------|-------|-------|-----------|
| Carbon | . . . | 72,02 | . . . | 69,0 | . . . | 72,0 | . . . | 44,71 | Analysis: |
| Oxygen | . . . | 14,84 | . . . | 20,0 | . . . | 17,0 | . . . | 49,69 | |
| Hydrogen | . . . | 7,61 | . . . | 6,5 | . . . | 5,5 | . . . | 5,59 | |
| Nitrogen | . . . | 5,53 | . . . | 4,5 | . . . | 5,5 | . . . | 0,06 | |
| | | 100,† | | 100,‡ | | 100,§ | | 100, | |

1915. *Meconic Acid*.—In opium, morphia is combined with a peculiar acid, which has been called meconic acid,¶ and was procured by M. Robiquet from the magnesian precipitate above mentioned, after the morphia had been separated from it.

The following process is said to afford pure meconic acid: Boil infusion of opium with magnesia, and digest the precipitate in alcohol; *meconiate of magnesia* remains; dissolve this in dilute sulphuric acid, and add muriate of baryta, a precipitate falls, composed of sulphate and *meconiate of baryta*; digest this in dilute sulphuric acid, which decomposes the meconiate: filter and evaporate, till brown crystals of impure meconic acid are deposited; dry these crystals, and then heat them carefully in a retort, to sublime the meconic acid. White crystals are thus obtained, which fuse at 250°, and sublime without decomposition; they are sour, and very soluble in water and alcohol.

Dr Hare has given the following process:** To an aqueous infusion of opium add sub-acetate of lead, collect the meconiate of lead by a filter, and expose it to sulphuretted hydrogen; the meconic acid will be set free. The solution is of a reddish amber colour, and furnishes, by evaporation, crystals of the same hue. Instead of sulphuretted hydrogen, sulphuric acid may be used to liberate the meconic acid.††

1916. Meconic acid has a sour, followed by a bitter taste, reddens litmus paper, and is very soluble both in water and alcohol. It is characterized by giving a red colour to a salt of the peroxide of iron, and communicates an emerald green tint to the sulphate of copper.

Dr Hare has founded a process for detecting minute quantities of opium in solution, on the property which meconic acid has of precipitating with lead. It consists in precipitating the meconic acid with acetate of lead, the meconic acid is liberated from the

* Tinctures of opium, it is observed by Sertuerner, should be prepared with pure alcohol, and kept in a place which is not very cold; for a low temperature precipitates morphia. The addition of a little acetic acid prevents this inconvenience. H.

† Pelletier and Dumas.

‡ Bussy.

§ Brande.

|| Thomson.

¶ From *Микон papaver*.

** *Amer. Jour.* xii. 293.

†† For a full account of opium, its constituent principles, &c. see a paper by Mr Carpenter in *Amer. Jour.* xiii. 17.

lead by sulphuretted hydrogen or sulphuric acid, to which add a solution of the sulphate of iron, which produces a striking red colour. Dr Hare observes, that a quantity of opium, not exceeding ten drops of laudanum may be detected in a half gallon of water.

Meconiate of morphia. 1917. *Meconiate of Morphia* may be obtained by the following process.

Reduce good opium to powder, put it upon a paper filter, add distilled water to it, and slightly agitate it; in this way wash it till the water passes through colourless; then pass a little diluted alcohol through it; dry the insoluble portion in a dark place; digest it in strong alcohol for a few minutes, applying heat; separate the solution, which, by cooling and subsequent evaporation, will yield the crystallized meconiate of a pale straw colour.*

Narcotine. 1918. *Narcotine*.—This substance, though not regarded as a vegetable alkali, may be noticed in this connection. It was described in 1803 by Derosne, and was long known by the name of the *Salt of Derosne*; M. Robiquet proved that it is a distinct principle, and applied to it the name of *narcotine*. It may be obtained pure by the following process of Mr Carpenter.†

Process for obtaining. Digest one ounce of coarsely powdered opium in one pint of ether for ten days, frequently submitting it to ebullition in a water bath; separate the ether, and add fresh portions, until the opium is exhausted; evaporate at the common temperature of the atmosphere, by placing the ethereal solution in a salt mouth bottle, remove the stopper, and cover the mouth with bibulous paper, to prevent impurities falling in, and protract the degree of evaporation; as the ether is reduced, it leaves the sides of the bottle coated with crystals of narcotine; as the solution becomes more dense the crystals enlarge and accumulate, and the bottom of the vessel is covered with large transparent crystals, accompanied with a brown viscid liquor and extract, which contains an acid, resin, caoutchouc, &c.; separate these substances from the crystalline mass, and wash the salt in successive portions of cold ether, to remove the extract. After the crystals have been sufficiently washed, dissolve them in warm ether and evaporate slowly as before, when most beautiful snow white crystals of perfectly pure narcotine will adhere to the sides of the vessel; those on the sides of the bottle assume plumose and arborescent forms, which being made up of delicate acicular crystals of a silky lustre, possess a most beautiful appearance. As the ethereal solution becomes more dense by a concentration of the narcotine, the crystals enlarge, and the bottom of the vessel, as before, is covered with perfectly pure narcotine, assuming the rhomboidal prismatic form, with some beautiful modifications of macle crystals; the crystals at the bottom and sides approaching the bottom, are perfectly transparent, while the most minute at the top are opaque being snow white. By picking out the largest and most regular crystals, and again dissolving them and evaporating and repeating the same process, each time selecting the largest and best crystals, perfect crystals one eighth of an inch in diameter may be obtained.‡

Properties. 1919. Pure narcotine is insoluble in cold and very slightly soluble in hot water. It dissolves in oil, ether, and alcohol, the latter though diluted acting as a solvent for it by the aid of heat. It does not possess alkaline properties, though it is rendered soluble in water by means of an acid.§

Strychnia. 1920. *Strychnia*.—M. M. Pelletier and Caventou, in analyzing the *bean of St. Ignatius* (*Strychnos Ignatia*), and the *vomica nut* (*Strychnos nux vomica*), discovered in them a

* *Quart. Jour.*

† *Amer. Jour.* xiii. 27.

‡ *Ibid.* p. 27.

§ The unpleasant stimulating properties of opium are attributed to the presence of narcotine; and Dr Hare has given a process for preparing denarcotized laudanum in *Amer. Jour.* xii. 291.

peculiar principle, which they have termed *Strychnine*, and which, like morphia, possesses alkaline properties. The following is their process for obtaining it:

Digest the raspings of the bean in sulphuric ether, which separates a green oily fluid; pour this off, and treat the residuum with alcohol; filter the latter solution when cold, and evaporate; it leaves a brown bitter substance, soluble in water and alcohol; to its strong aqueous solution add a solution of potassa, which causes a precipitate, which, when washed with a little cold water, is white, crystalline and very bitter. If not quite pure, it may be rendered so by solution in acetic acid, and precipitation by potassa.

1921. *Strychnine*, or *Strychnia*, is nearly insoluble in water; it dissolves in alcohol, and the solutions are intensely bitter and poisonous. It reproduces the blue of vegetable colours reddened by acids. It crystallizes in small quadrangular prisms; it has no smell; is neither fusible nor volatile, and is composed of 6,38 oxygen, 6,54 hydrogen, 78,22 carbon, and 8,92 nitrogen.*

1922. The discoverers of strychnia assert that it exists in the above-mentioned seeds, combined with a peculiar acid, somewhat resembling the malic, but susceptible of crystallization; they have called it *Igasuric Acid*, and the poisonous principle existing in the seeds, appears to be an *igasurate of strychnia*.

1923. *Brucia*.—This term has been applied to a peculiar alkaline substance, obtained from *Angustura bark*, by the above-named chemists. Its properties, as far as they have been investigated, are described in the *Annales de Chimie*, (xii. p. 113.) and in the *Quarterly Journal of Science and the Arts*, (ix. 189.)

1924. *Delphia* is an alkaline principle, discovered by MM. Lassaigne and Feneulle in the seeds of stavesacre (*Delphinium Staphysagria*). It possesses the general characters of the vegetable alkalies.†

1925. *Picrotoxia*.—The bitter poisonous principle of the *Cocculus indicus* was discovered in 1819 by M. Boullay, who gave it the name of *picrotoxine*. Its claim to the title of a vegetable alkali, has been called in question by M. Casaseca, from whose remarks it seems that picrotoxia has no alkaline reaction, and does not neutralize acidity. It combines, however, with acids, and with the acetic and nitric acids forms crystallizable compounds. It appears, also, that the menispermic acid, supposed by M. Boullay to be united in the *cocculus indicus* with picrotoxia, is merely a mixture of the sulphuric and malic acids.‡

* The Salts of *Strychnia* are decomposed by potassa, soda, ammonia, baryta, strontia, and magnesia, the base being thrown down; most of the other metallic salts are decomposed by strychnia, and with some it forms triple salts.

Sulphate of Strychnia forms cubic crystals, soluble in about 10 parts of water at 60°; its taste is bitter, and it is decomposed by the alkalies. It consists of sulphuric acid 9,5 strychnia 90,5.

Nitrate of Strychnia is formed by digesting excess of strychnia in very dilute nitric acid; it yields stellated crystals, which acquire a red colour by the action of sulphuric acid. Nitric acid poured upon strychnia or its salts produces a deep red colour.

† *Annales de Chimie et Phys.* xii. 359.

‡ *Edin. Jour. of Sci.* x.

Solania.

1926. *Solania*.—The active principle of the *solanum dulcamara* or woody nightshade, was procured in a pure state by Desfosses. It has distinct alkaline properties.*

M. Peschier has discovered an acid in the *solanum nigrum*, which he has called *solanic acid*, combined with solania†

1927. *Conia* is the active principle of Hemlock, *conium macculatum*.

It is obtained by digesting the fresh plant for several days in alcohol, filtering, and evaporating the liquid, mixing the residue with water, and acting either by alumina, magnesia, or the oxide of lead; the whole is then to be evaporated to dryness, and the substance obtained acted upon by a mixture of alcohol and ether; the solution being evaporated, yields *Conia*.

Its aqueous solution forms an abundant red precipitate with tincture of iodine. Half a grain of it will kill a rabbit, the symptoms being the same as those produced by strychnia.‡

Corydalin.

1928. *Corydalin* is a new alkali discovered by M. Wackenroder, in the root of the fumitory, *fumaria cava*, and *corydalis tuberosa* of Decandolle. It is soluble in alcohol, and crystallizes in prisms. It forms extremely bitter salts with acids. Tannin is one of the most sensible tests of corydallin; the precipitate is white when the solution is dilute, and grayish yellow if concentrated.§

Piperine.

1929. *Piperine* is the active principle of black pepper, and may be obtained from an ethereal solution in straw coloured prismatic crystals.||

SECTION XV. Bitumens, Coal, &c.

Bitumens.

1930. Though bitumens, on account of their origin, are, with more propriety, classed among mineral substances; yet, in chemical properties, they are more closely allied to the products of the vegetable kingdom. Like vegetable substances in general, they burn in the open air, and with a degree of brightness that surpasses even that of resins. By distillation *per. se*, they yield a weak acetic acid, an empyreumatic oil, some ammonia, and a considerable quantity of carburetted hydrogen gas, with occasionally a small proportion of carbonic acid and sulphuretted hydrogen. They are neither soluble in water nor in alcohol, and in the latter respect they differ from resin. There can be little doubt that they have been formed originally by the decomposition of vegetables.

How divided.

1931. The bitumens have been divided into liquid and solid. Formerly it was supposed that the liquid bitumens had been derived, by a sort of natural distillation, from the solid; but Mr Hatchett has rendered it more probable, that the solid bitumens result from the consolidation of the fluid ones.

* Jour. de Pharm. vi. and viii.

† Quart. Jour. N. S. v. 227.

‡ Bull. Univ. c. xii. 253.

§ Philos. Mag. &c. xx. 151.

|| See a process for obtaining, and remarks on the use of this substance, by Mr Carpenter in Amer. Jour. xiii. 326.

The bituminous substances are Naphtha, Petroleum, Mineral Tar, Mineral Pitch, Asphaltum, Jet, Pit-Coal, Bituminous wood, Turf, and Peat. To these, some writers have added Amber and the Honey-Stone.

a. Naphtha is a pungent, odoriferous, oily liquid, either colourless or of a pale brown tint, found upon the borders of the Caspian Sea, and in certain springs in Italy. It is considerably lighter than water, volatile, and highly inflammable. When pure it appears to contain no oxygen, and hence is employed for the preservation of potassium, and the other highly oxidable metals. It consists, according to Saussure, of

| | | | |
|----------|-----------|------------|----------|
| Carbon | | 87,21 | Analysis |
| Hydrogen | | 12,79 | |
| | | <hr/> 100, | |

This would indicate

| | | | | |
|-------------------|-----------|----------|-----------|-----------|
| 6 atoms of carbon | | 36 | | 32 |
| 5 " " hydrogen | | 5 | | 12 |
| | | <hr/> 41 | | <hr/> 100 |

Dr Ure's analysis would give 20 atoms of olefant gas, + 1 of carbonic oxide + 1 of free carbon. H. 2. 316.

1932. *Naphthaline*.—This substance, is one of the products of the decomposition of coal. If the distillation be conducted at a very gentle heat, naphtha from its greater volatility, first passes over, and afterwards naphthaline rises in vapour, and condenses in the neck of the retort as a white crystalline solid.*

Pure naphthaline is heavier than water, has a pungent aromatic taste, and a peculiar odour not unlike that of the narcissus. It is smooth and unctuous to the touch, is perfectly white, and has a silvery lustre. It fuses at 180° F. volatilizes slowly at common temperatures, and boils at 410° F. It is not very readily inflamed, but when set on fire it burns rapidly, and emits a large quantity of smoke. It is insoluble in cold, and dissolves very sparingly in hot water. Its proper solvents are alcohol and ether.

Sulphuric acid enters into direct combination with naphthaline, and forms a new and peculiar acid, which Mr Faraday has described under the name of *sulpho-naphthalic acid* †

Naphthaline according to Dr Thomson is a *sesquicarburet of hydrogen*, that is, a compound of 9 or an atom and a half of carbon and 1 atom of hydrogen:‡

b. Petroleum has most of the properties of naphtha, but is less fluid, and darker coloured. In the countries where it abounds, it is employed for burning in lamps.

c. Mineral Tar appears to be petroleum further inspissated. It is more viscid, and of a deeper colour.

d. Maltha, or Mineral Pitch, is a soft inflammable substance, heavier than water, and may be considered as derived from the exsiccation of mineral tar.

* Kid in *Philos. Trans.* 1821. † *Ibid.* 1826. ‡ *First Principles*, i. 156.

Asphaltum.

e. Asphaltum is found abundantly on the shores of the Dead Sea, in Albania, and in the island of Trinidad. Its colour is brown or black; it is heavier than water, and readily soluble in naphtha.

Elastic bitumen.

f. Elastic Bitumen, or *Mineral Caoutchouc*, is found in the vicinity of Castleton, Eng. and at Southbury in the state of Connecticut.* It is fusible and inflammable.

g. Mineral Adipocere is a fatty matter found in the argillaceous iron ore of Merthyr: it is fusible at about 160°, and inodorous when cold, but of a slight bituminous odour when heated, or after fusion.

The above substances are insoluble in water, and difficultly soluble in alcohol, with the exception of naphtha and petroleum, which are soluble in highly rectified alcohol.

Retinasphaltum.

h. Retinasphaltum is a substance which accompanies the Bovey Coal of Devonshire. It was first analyzed by Mr Hatchett, who found it to consist of

55 Résin.

41 Asphaltum.

4 Earthy matter and loss.

Pit Coal.

i. Pit coal.—There are three chemical varieties of this important substance. The first, or *brown coal*, retains some remains of the vegetables from which it has originated. When heated it exhales a bituminous odour, and burns with a clear flame. It is generally of a tough consistency, and yields according to Mr Hatchett, a portion of unaltered vegetable extract, and resin.

The second variety, or *black coal*, is the ordinary fuel of Great Britain. It exhibits no traces of vegetable origin, and consists principally of bitumen and charcoal, in variable proportions. When exposed to heat, it swells, softens, and burns with a bright flame, leaving a small quantity of ashes. Many varieties, however, abound in earthy matter, and these produce copious cinders, and burn with a less intense heat.

The products of the destructive distillation of this kind of coal have been already described. The residue is a hard sonorous charcoal, termed *coke*, and containing the earthy ingredients of the coal.

The third variety, *glance coal* or *anthracite*, consists almost entirely of charcoal, and earthy matter.

It usually burns with little flame† and when submitted to distillation yields no tar, and a sort of carburetted hydrogen gas.

Peat.

k. Peat and *Turf* consist principally of the remains of vegetables, having undergone comparatively little change. They often contain bituminous wood, and branches and trunks of trees.

Mellite.

l. Mellite, or *Honeystone*, is a rare substance, found in the brown coal of Thuringia and in Switzerland. It is of a honey

* *Amer. Jour.* vi. 370.† Some of the anthracite of this country burns with considerable flame, see *Amer. Jour.* x. 336.

yellow colour, crystallized in octoëdra, and when analyzed by Klaproth, was found to consist of alumina combined with a peculiar body which has been called the *mellitic acid*.*

SECTION XVI. Vegetable Acids.

1933. The following are the principal acids, which are found ready formed in vegetable products :

1. Tartaric acid.

2. Oxalic acid.

3. Citric acid.
4. Malic acid.

5. Gallic acid.

6. Benzoic acid.

i. TARTARIC ACID.

1934. This acid exists in several vegetable substances ; it is one of the sour principles of many fruits, and is said to be abundant in the potato-apple. Tartaric acid is generally obtained from the *bi-tartrate of potassa*, (*purified cream of tartar*.)

Sources.

Mix 100 parts of this salt in fine powder with 30 of powdered chalk, and gradually throw the mixture into 10 times its weight of boiling water : when the liquor has cooled, pour the whole upon a linen strainer, and wash the white powder which remains with cold water : this is a *tartrate of lime* ; diffuse it through a sufficient quantity of water, add sulphuric acid equal in weight to the chalk employed, and occasionally stir the mixture during 24 hours ; then filter, and carefully evaporate the liquor to about one-fourth its original bulk ; filter again, and evaporate with much care nearly to dryness ; re-dissolve the dry mass in about 6 times its weight of water, render it clear by filtration, evaporate slowly to the consistency of sirup, and set aside to crystallize.

Mode of obtaining.

By two or three successive solutions and crystallizations, tartaric acid will be obtained in colourless crystals, soluble in 6 parts of water at 60°. Their primary form is an oblique rhombic prism.†

1935. The crystals melt at a heat a little exceeding 212° into a fluid which boils at 250° and leaves a semi-transparent mass on cooling, slightly attractive of moisture from the air, though the original crystals were not deliquescent. The dry acid consists of

Properties.

| | | |
|----------------------|------------|-----------------|
| 4 Carbon | 6 × 4 = 24 | } 66 Berzelius. |
| 5 Oxygen | 8 × 5 = 40 | |
| 2 Hydrogen | = 2 | |

Analysis.

The crystals contain 1 proportion of water.

The aqueous solution of tartaric, in common with the other vegetable acids, soon becomes mouldy, and suffers decomposition.

1936. When tartaric acid is submitted to destructive distillation, it affords a brown acid liquor which has been termed *pyrotartaric acid*.

Pyrotartaric acid.

* Klaproth's *Essays*, ii. 89. Vauquelin, *Annales de Chimie* xxxvi. 203.
‡ Brooke in *Ann. Philos.* vi. N. S.

Characters of
the tartrates.

1937. Tartaric acid is remarkable for its tendency to form double salts, the properties of which are often more interesting than those of the simple salts. The most important of these double salts, are the tartrate of potassa and soda, and the tartrate of antimony and potassa. The neutral tartrates of the alkalies, of magnesia and copper, are soluble in water; but most of the tartrates of the other bases, and especially those of lime, baryta, strontia, and lead are insoluble. All these neutral tartrates, however, which are insoluble in pure water, are soluble in an excess of their acid. They are decomposed by digestion in carbonate of potassa, and when an acid is added in excess, the bi-tartrate of potassa is precipitated. All the insoluble tartrates are easily procured from the neutral tartrate of potassa by way of double decomposition. T.

Tartrate of
potassa.

1938. *Tartrate of Potassa*, (formerly *soluble tartar*) is formed by saturating the excess of acid in *tartar*, by potassa. According to Mr Richard Phillips,* 100 parts of tartar require 43.5 of sub-carbonate of potassa. The resulting salt is soluble in less than twice its weight of water; it forms large crystals, the primary form of which is a right oblique angled prism.† These contain 2 atoms of water: when anhydrous it consists of

$$\begin{array}{rcl} 1 \text{ proportional acid} & . & . & . & . & . & = 66. \\ 1 & . & . & . & . & . & \text{potassa} & . & . & . & . & = 48. \end{array}$$

$$\text{Tartrate of potassa} \quad . \quad . \quad . \quad . \quad . \quad . \quad = 114.$$

This salt is used in pharmacy as an aperient; it is the *potassæ tartras* of the *Pharmacopœia*. Its taste is saline, and somewhat bitter.

Bitartrate, or
crude tartar.

1939 *Bi-tartrate*, or *Supertartrate of potassa*. *Tartar*. This substance exists in considerable abundance in the juice of the grape, and is deposited in wine casks, in the form of a crystallized incrustation; called *argol* or *crude tartar*. It is purified by solution and crystallization, which renders it perfectly white: when in fine powder it is termed *cream of tartar*.

Tartaric acid
test for potas-
sa,

It may also be formed by adding excess of tartaric acid to a solution of potassa. The mixture presently deposits crystalline grains, and furnishes a striking example of the diminution of solubility by increase of acid in the salt. Upon this circumstance the use of tartaric acid as a test for potassa depends, for soda forms an easily soluble supertartrate and consequently affords no precipitate.

Bi-tartrate of potassa is composed of

2 proportionals of acid, 1 proportional of potassa.

contains wa-
ter.

1940. In the bi-tartrate, is also found a quantity of water which appears essential to the constitution of the salt; for it cannot be separated by heat, without decomposing the acid. Its proportion is 2 atoms.

Bi-tartrate of potassa, it is observed by Gay-Lussac,‡ acts, in many cases, like a simple acid, and even dissolves oxides that

* Remarks on the Pharmacopœia.

† Brooke in *Ann. Phils.* vii. 161.

‡ *Ann. de Chim. et Phys.* iii. 281.

are insoluble in the mineral acids and in the tartaric acid. He proposes its use, therefore, in mineral analysis. H.

1941. When exposed to heat, tartar fuses, blackens, and is decomposed: and carbonate of potassa is the remaining result. Provided the tartar be free from lime, which however is seldom the case, this furnishes a good process for obtaining pure carbonate of potassa. The aqueous solution of tartar becomes mouldy when exposed to air, and the tartaric acid being entirely decomposed leaves a weak solution of carbonate of potassa.

Effect of heat.

The component parts of tartar render it an excellent flux in the reduction of metallic ores upon a small scale, its alkali promoting their fusion, and the carbonaceous matter tending to reduce the oxides.

1942. *Tartrate of Potassa and Soda* is prepared by saturating the excess of acid in tartar, with carbonate of soda; it is the *tartras potassæ et sodæ* of the *Pharmacopœia*; it forms prismatic crystals.* It has long been used in pharmacy under the name of *Rochelle Salt* and *Sel de Seignette*. It consists of 1 atom of the tartrate of potassa, 1 atom of the tartrate of soda, and 8 atoms of water. T.

Tartrate of potassa and soda.

It is frequently made extemporaneously by dissolving equal weights of tartaric acid and the bi-carbonate of soda in separate portions of water, and then mixing the solutions.†

1943. *Tartrate of Iron and Potassa*—This is the *Ferrum tartarisatum* of the London *Pharmacopœia*, but it is most conveniently employed as a medicine in solution, which may be formed by digesting 1 part of soft iron filings with 4 of tartar; this mixture should be made into a thin paste with water, and digested for some weeks, till the acid is neutralized, fresh portions of water being occasionally added to prevent exsiccation. The solution of this compound which contains the iron in the state of peroxide, is possessed of some curious properties, first pointed out by Mr R. Phillips.‡

— of iron and potassa.

1944. *Tartrate of Potassa and Copper* is formed by boiling oxide of copper and tartar in water: the solution yields blue crystals on evaporation; or if boiled to dryness, furnishes one of the pigments called *Brunswick green*.

1945. *Tartrate of Antimony and Potassa. Emetic Tartar*.—This compound may be obtained by boiling protoxide of antimony, with pure supertartrate of potassa. It is the *antimonium tartarizatum* of the London and U. S. *Pharmacopœia*.

— of antimony and potassa.

Emetic tartar may be prepared by boiling a solution of 100 parts of tartar with 100 parts of finely levigated glass of antimony, or of the protoxide described above (1390); the ebullition should be continued for half an hour, and

Preparation of emetic tartar.

* The forms of its crystals arising from the modification of a right rhombic prism, are represented by Mr Brooke in *Ann. Philos. N. S. v. 451*.

† *Soda* or *Sodaic* powders of the shops are packed in two distinct papers, the one blue and the other white, the blue containing half a drachm of carbonate of soda, the white gr. xxv of tartaric acid; when dissolved and mixed, effervescence takes place but the liquid is by no means similar to "soda water."

‡ *Experimental Examination of the London Pharmacopœia*, 98.

the filtered liquor evaporated to about half its bulk, and set aside to crystallize : octoëdral and tetraëdral crystals of the emetic salt are thus obtained ; and there is generally formed along with them a portion of tartrate of lime and potassa, which is deposited in small tufts of a radiated texture, and which may easily be separated when the mass is dried.

Mr Phillips, in his *Experimental Examination of the London Pharmacopœia*, has stated several facts respecting the formation of this salt, which will be found useful to the manufacturer.*

Properties.

Emetic tartar is a white salt, slightly efflorescent, soluble in about 14 parts of cold and 2 parts of boiling water. It is decomposed by the alkalies, and when heated with ammonia, a portion of protoxide of antimony is thrown down, and a very soluble compound remains in the liquor. Sulphuretted hydrogen and hydrosulphuret of ammonia produce orange-coloured precipitates in its solution.† It is decomposed by bitter and astringent vegetable infusions, but they do not render it inactive as a medicine.‡ In a late analysis Mr Phillips has shown that emetic tartar consists of

Analysis.

| | |
|--|-------|
| Bi-tartrate of potassa (anhydrous) | 49,25 |
| Protoxide of antimony | 43,35 |
| Water | 7,40 |

100.

and he considers it as composed of 1 atom of bi-tartrate of potassa, 3 atoms of protoxide of antimony, and 3 atoms of water.§

According to the analysis of Dr Thomson emetic tartar consists of 2 atoms tartaric acid, 3 atoms protoxide of antimony, 1 atom of potassa and 2 atoms of water.

ii. OXALIC ACID.

● Oxalic acid.

1946. This acid is found in some fruits, and in considerable quantity in the juice of the *Oxalis Acetosella*, or wood-sorrel, and in the varieties of *rhubarb*.|| It is most readily procured by the action of nitric acid upon sugar, and has hence been termed *acid of sugar*.

How obtained.

It may be obtained by introducing into a retort 4 ounces of nitric acid diluted with 2 of water and 1 ounce of white sugar ; nitric oxide gas is copiously evolved, and when the sugar has dissolved, about one-third of the acid may be distilled over : the contents of the retort are then emptied into a shallow vessel, and in the course of two or three days an abundant crop of white crystals is deposited, and, upon further evaporation of the mother-liquor, a second portion is obtained. The whole crystalline produce is to be redissolved in water, and again crystallized, by which the pure acid is obtained. In this way sugar yields rather more than half its weight of oxalic acid.

* See Bigelow's *Sequel*, 75.

† According to Dr Turner (*Brewster's Jour.* xv. 174.) sulphuretted hydrogen is a very certain test of the presence of emetic tartar in mixed fluids.

‡ According to Orfila the compound of tannin and oxide of antimony is inert, and he recommends a decoction of cinchona bark as an antidote.

§ *Mag.* lxx. 379.—For other tartrates, see Henry's *Chemistry*, ii. 233.

|| M. Braconnot has lately found it in great quantity in combination with lime, in most species of lichens. See his Memoir in the *Ann. de Chim.* xxviii. 318 and *Quart. Jour.* xix. 353.

M. Braconnot obtained oxalic acid by the following process from lichens.

The lichen reduced to powder was boiled with carbonate of soda, the filtered liquor was saturated with nitric acid, and acetate of lead was added, the precipitate was decomposed by sulphuric acid; and, a nearly colourless solution was obtained from which crystals of oxalic acid separated. Another portion was afterwards separated from the residue left by the carbonate of soda.*

1947. Oxalic acid has the form of an oblique rhombic prism. Characters.
The crystals are transparent, and of a very acid taste: they dissolve in two parts of water at 60°, and in their own weight at 212°. They are soluble also in boiling alcohol, and sparingly in ether. The crystals effloresce in the air; and a red heat decomposes them. During distillation, a considerable quantity of inflammable gas is obtained, and a portion of the acid is sublimed, unaltered, into the neck of the retort.

1948. Oxalic acid is decomposed both by the oxides and chloride of gold, and in the former case with a disengagement of carbonic acid.† Decomposed by gold.

Dry oxalic acid, according to Dobereiner consists of

| | | | |
|----------------|-----------|---------------------|--------------|
| 2 Carbon . . . | = 12 or 1 | Carbonic oxide = 14 | Composition. |
| 3 Oxygen . . . | = 24 “ 1 | “ acid = 22 | |
| | 36 | 36 | |

The crystallized acid, according to Dr Thomson consists of 1 dry acid + 4 water.

1949. This acid is a most virulent poison, and from the resemblance which the crystals bear to those of Epsom salt, many fatal mistakes have arisen. The acid taste is in itself a sufficient mark of distinction; or without tasting it, if a few drops of water be placed on a slip of the dark blue paper which is commonly wrapped round sugar loaves, and a small quantity of the suspected crystal be added, if it be oxalic acid it will change the colour of the paper to a reddish brown. The solution also of a small quantity of this acid in a tea-spoonful of water, will effervesce with a little scraped chalk or whiting. H.—When the acid has been swallowed, copious draughts of lime water, or magnesia and water, should be administered, and vomiting excited as speedily as possible. How distinguished from Epsom salts.

1950. Oxalic acid is a good test for detecting lime, which it separates from all other acids, unless they are present in excess. Test of lime.

1951. *Oxalate of Ammonia* is a very useful test of the presence of lime. It crystallizes in long prisms, of which 45 parts require 1000 of water. Added to any soluble compound of lime this salt produces an insoluble *oxalate of lime*. Oxalate of ammonia.

* The same chemist has employed the following process; 100 parts of the pulverized lichen were boiled with 33 parts of sulphuric acid and a sufficient quantity of water, for half an hour, filtered to separate the sulphate of lime, and the liquid was carefully evaporated avoiding the reaction of the excess of sulphuric acid on the oxalic acid. When cold it became crystalline, and by pressure in bibulous paper 17 parts of yellowish white oxalic acid were obtained, some still remaining dissolved. *Ann. de Chim.* xxviii. 318.

† *Ann. de Chim. et Phys.* xv. 125.

— of potassa. 1952. *Oxalate of Potassa* forms flat oblique four-sided prisms, terminated by dihedral summits, the lateral edges of the prism being usually bevelled. Its taste is cooling and bitter. At 60° F. it requires about twice its weight of water for solution. There is also a salt, formed of the same base and acid, but with a considerable excess of acid, called *super-oxalate* or *bin-oxalate of potassa*. It forms small white parallelipeds or rhomboids approaching to cubes. It has a pungent acid taste mixed with some bitterness. It requires for solution ten times its weight of water at 60°, and a still larger proportion of boiling water. It may either be formed artificially, or obtained from the juice of the *oxalis acetosella*, or of the *rumex acetosa*. When procured in the latter mode, it is sold under the name of *salt of sorrel*, or *essential salt of lemons*. The acid, which it contains, is double that in the oxalate.

Salt of Lem-
ons.

According to Berzelius, 100 parts of potassa are united, in the oxalate, with 76,58 parts of real oxalic acid, and in the binoxalate, of course, with 153,16. Exclusively of water, which in the crystals of the oxalate, amounts to 17,31 per cent. they are composed as follows:

| | Acid. | Base. |
|--------------------------|---------------|-------|
| Oxalate of potassa . . . | 43,37 | 56,63 |
| Binoxalate of ditto. . . | 60,47 | 39,53 |

M. Serullas finds that when dry and pure oxalate of potassa, either acidulous or neutral, is finely powdered with an equal weight of antimony and heated in a forge fire for 8 or 10 minutes in a covered crucible, there is always procured an alloy of potassium and antimony.

Quadroxa-
late of potas-
sa.

1953. *Quadroxalate of Potassa* may be composed by several methods.* It was formed by Dr Wollaston, by digesting the bin-oxalate in nitric or muriatic acid. The alkali is divided into two parts, one of which unites with the mineral acid, and the other half remains in combination with the oxalic acid. It forms beautiful crystals, which may be obtained pure by solution and a second crystallization.

If three parts by weight of the quadroxalate be decomposed by burning, and the alkali, which is thus disengaged, be mixed with a solution of one part of the crystallized salt, the latter is exactly neutralized. Hence the quadroxalate contains four times the acid that exists in the oxalate. The analysis of this class of salts, from which Dr Wollaston (in the *Phil. Trans.* for 1808) drew a striking exemplification of the law of simple multiples discovered by Mr Dalton, may be recapitulated as follows:

| Composition. | Atom of base. | Atoms of acid. | Base. | Acid. | Equivalent Number. |
|-------------------------|------------------|-------------------|-------|-------|-----------------------|
| The oxalate consists of | 1 + | 1 | 48 + | 36 = | 84 |
| The binoxalate | 1 + | 2 | 48 + | 72 = | 120 |
| The quadroxalate . . . | 1 + | 4 | 48 + | 144 = | 192 |

* See Berard, 73 *Ann. de Chim.* 271.

Estimating, therefore, from the weights of their atoms, 100 of potassa should be united, in the oxalate, with 75 of acid; in the binoxalate, with 150; and in the quadroxalate, with 300. H. 2. 204.

1954. When black oxide of manganese and superoxalate of potassa are triturated together and moistened, carbonic acid is evolved; and on adding more water, and filtering, a red solution, containing oxalic acid, potassa, and deutoxide of manganese is obtained, which after a time becomes colourless, and a triple salt is formed, containing the protoxide of manganese.

1955. *Oxalate of Lime*—This compound is formed by adding oxalic acid or oxalate of ammonia to any solution of lime. It is insoluble in water, and in excess of oxalic acid, but dissolves in muriatic and nitric acids: hence in testing acid solutions for lime by oxalic acid, or oxalate of ammonia, the excess of acid should be previously neutralized. This oxalate, dried in the temperature of 95° Dr Thomson finds is composed of 1 atom oxalic acid, 1 lime, and 2 atoms of water.—The anhydrous salt consists of

Oxalate of lime.

| | | | |
|-----------------------|------------------|--------------|-------|
| Lime | 1 atom | 28 | 43,75 |
| Oxalic acid | 1 | 36 | 56,25 |
| | | 64 | 100,* |

Composition.

1956. *Oxalate of Iron*.—The *proxoxalate* crystallizes in green prisms, and may be formed either by digesting the metal, or dissolving the protoxide in the acid. The *peroxalate* is thrown down from the permuriate or persulphate of iron, in the form of a difficultly soluble yellow powder, which is taken up again by excess of oxalic acid: hence the use of this acid in removing iron-moulds which it does without injuring the texture of linen.

Of iron.

1957. *Oxalate of Copper and Ammonia*.—This and several other triple oxalates of copper have been described by Vogel.† By digesting peroxalate of copper in a solution of oxalate of ammonia and filtering, rhomboidal crystals were obtained on evaporation, which detonate when suddenly heated: when slowly heated they merely lose water and ammonia. From the analysis of this salt it evidently consists of 2 proportionals of oxalate of ammonia, 1 peroxalate of copper, and 6 water.

Of copper and ammonia.

By digesting oxalate of copper in caustic ammonia, and pouring the solution thus obtained into a shallow basin, it deposits flat six-sided prisms of a blue colour, which effloresce on exposure to air. The undissolved portion of the oxalate also combines with ammonia, and produces another distinct compound.

1958. *Oxalate of Lead* is best formed by adding oxalic acid to solution of nitrate, or acetate of lead. It is composed, according to Berzelius, of 24,54 acid + 75,46 oxide of lead.‡

* *Oxalate of Soda* is sparingly soluble in water, and separates from its solution in small crystalline grains. † Schweigger's *Journal*, vii. ‡ For other oxalates see Henry's *Chemistry*, ii. 207.

When well dried oxalate of lead, mixed with very small portions of potassium, perfectly freed from naphtha, is put into the bottom of a glass tube, the air being carefully excluded, by excess of the oxalate, a violent detonation suddenly takes place before the heat is sufficiently great to effect the decomposition of the oxalate, when no potassium is present. The tube is spotted with metallic lead, the potassium is oxidized, and there is no carbon deposited.*

iii. CITRIC ACID.

1959. Citric acid is obtained by the following process from lemon or lime juice :

How prepared.

Boil the expressed juice for a few minutes, and when cold, strain it through fine linen ; then add powdered chalk as long as it produces effervescence, heat the mixture, and strain it as before : a quantity of citrate of lime remains upon the strainer, which, having been washed with cold water, is to be put into a mixture of sulphuric acid with 20 parts of water : the proportion of acid may be about equal to that of the chalk employed. In the course of 24 hours the citrate of lime will have suffered decomposition, and sulphate of lime is formed, which is separated by filtration. The filtered liquor, by careful evaporation, as directed for tartaric acid, furnishes crystallized citric acid.†

The preparation of this acid is carried on by a few manufacturers upon an extensive scale ; in different states of purity it is employed by the calico-printers, and used for domestic consumption. Many circumstances which have not here been alluded to, are requisite to ensure complete success in the operation ; these have been fully described by Mr Parkes, in the third volume of his *Chemical Essays*. The proportion of citric acid afforded by a gallon of good lemon-juice, is about 8 ounces.

Characters.

1960. Citric acid forms crystals of a very sour taste, soluble in their own weight of water at 60°, and containing, according to Berzelius, 1 atom real acid + 2 atoms water, a portion of which it loses by exposure to heat.

1961. From the analysis of citrate of lead, the representative number of citric acid appears to be a number which closely corresponds with Berzelius's estimate of its constitution, which is

| | | | |
|---|-----------------------------------|---|----------|
| 4 | Proportionals of oxygen | 8 | × 4 = 32 |
| 2 | ————— hydrogen | 1 | × 2 = 2 |
| 4 | ————— carbon | 6 | × 4 = 24 |
| | | | — |
| | | | 58 |

1962. Exposed to heat, the crystals undergo the watery fusion, and the acid itself is decomposed before all its water of crystallization is expelled. Besides the usual products of vegetable matter, a peculiar acid sublimes, to which the name of *pyro-citric acid* is applied.

* Oxalate of copper treated in the same way also occasions strong detonation, and metallic copper appears. *Jour. de Phar.* Nov. 1826.

† For a mode of obtaining it from goose-berries see *Ann. Philos.* N. S. iv. 152.

1963. Citric acid is characterized by its flavour, by the form of its crystals, and by forming an insoluble salt with lime, and a deliquescent soluble compound with potassa. It is chiefly employed as a substitute for lemon-juice.*

iv. MALIC ACID.

1964. The existence of a peculiar acid in the juice of apples, was shown by Scheele, in 1785. He obtained it by adding solution of acetate of lead to the expressed juice of unripe apples, by which a *malate of lead* was formed, and afterwards decomposed by sulphuric acid. Vauquelin obtained it by a similar process from the juice of the *house-leek*. The same acid exists, according to Braconnot, in the berries of the *mountain-ash*, from which it was first obtained by Mr Donovan in 1815, and called by him *sorbic acid*; the apparent differences between the malic and sorbic acids, are referable to the impurities of the former. Mr Donovan has given the following process for its preparation.†

Express the juice of the ripe berries, and add solution of acetate of lead, filter, and wash the precipitate with cold water, then pour boiling water upon the filter, and allow it to pass through the precipitate into glass jars; after some hours crystals are deposited, which are to be boiled with 2,3 times their weight of sulphuric acid, specific gravity 1,090. The clear liquor is to be poured off, and, while still hot, a stream of sulphuretted hydrogen is to be passed through it, to precipitate the remaining lead; the liquid is then filtered, and when boiled so as to expel the sulphuretted hydrogen, is a solution of the pure vegetable acid. Whence obtained.

Malic acid may also be obtained by steeping sheet-lead in the juice of apples; in a few days, crystals of malate of lead form, which may be collected and decomposed by the very careful addition of dilute sulphuric acid. Process.

1965. It may be formed, also, by the action of nitric acid on sugar.

Equal weights of sugar and nitric acid are to be distilled together, till the mixture assumes a brown colour. The oxalic acid may be separated by adding lime water; after which, the remaining liquor is to be saturated with lime and filtered. On the addition of alcohol, a coagulum of malate of lime is formed, which may be dissolved in water, and decomposed, as in the preparation of acetate of lead; and afterwards by sulphuric acid. This process however is extremely uncertain and costly. H.

1966. Malic acid, when carefully prepared, is a colourless liquid, very sour, and not susceptible of crystallization. It forms crystallizable salts with many of the metallic oxides, Properties.

* *Citrate of Potassa* is very soluble, deliquescent, and difficultly crystallizable. It is much used in medicine as a mild diaphoretic, and is the *Salt of Riverius* of old pharmacy.

Citrate of Soda is difficultly crystallizable in hexaëdral tables, of a saline flavour, and soluble in somewhat less than two parts of cold water.

Citrate of Lime has been adverted to in the preparation of citric acid. It is nearly tasteless, and scarcely soluble in water, but readily soluble in solution of citric acid: when moistened it soon grows mouldy if exposed to air. It consists of 1 proportional acid, and 1 lime.

The remaining citrates are of little importance.

† *Phil. Trans.* 1815.

which, however, have scarcely been examined with such precision as to enable us to determine the representative number of malic acid. A detailed account of what is known respecting them will be found in M. Braconnot's Memoir.* His analysis of the crystallized *malate of lead* gives its composition thus :

| | |
|-------------------------|-------|
| Acid | 100, |
| Oxide of lead | 157,4 |

When malic acid is heated out of the contact of air, it sublimes, and the sublimed crystals possess characters differing from those of the original acid. When thus altered, it has been called *pyromalic Acid*.

Sorbic acid. 1967. The *sorbic acid*, which may now be considered as identical with the malic, was analyzed by Vauquelin, by combustion with oxide of copper, and its composition is stated to be

| | |
|--------------------|------|
| Carbon | 28,3 |
| Oxygen | 54,9 |
| Hydrogen | 16,8 |

Analysis. 100,

These results indicate.

| | | |
|--------------------------------|----|-----------------|
| 3 atoms of carbon | 18 | 30, |
| 4 ditto of oxygen | 32 | 53,33 |
| 10 ditto of hydrogen | 10 | 16,67 |
| | 60 | 100. H. 2. 225. |

General properties of malates. 1968. Most of the salts of malic acid are more or less soluble in water. The malates of soda and potassa are deliquescent and very soluble. Those of lead and lime, the most insoluble of the malates, are sparingly soluble in cold water, but are freely dissolved by that liquid at a boiling temperature, a circumstance which distinguishes the malic from the oxalic, tartaric and citric acids. T.

V. GALLIC ACID.

1969. This acid derives its name from the *gall-nut*, whence it was first procured by Scheele. It may be obtained by the following process.

How obtained. Digest bruised galls in boiling water, with about one-sixth their weight of vellum cuttings, for some hours; then allow the mixture to cool, and filter it. Add to the filtered liquor a solution of acetate of lead, as long as it occasions any precipitate; pour the whole upon a filter, wash the precipitate with warm water, and digest it in very dilute sulphuric acid; filter, and having saturated the clear liquor with chalk, evaporate to dryness. Introduce the dry mass into a retort placed in a sand-bath, and upon the application of heat a portion of water will first rise, and afterwards a crystalline sublimate of gallic acid.

Other processes. There are many other processes for obtaining this acid, among which the following deserve notice: Moisten bruised gall-nuts, and expose them for four or five weeks, to a temperature of about 80°. A mouldy paste is formed, which is to be squeezed dry, and digested in boiling water; it then affords a solution of gallic acid, which may be whitened by animal charcoal, and which, on evaporation, yields gallic acid, crystallized in white needles.†

* *Annales de Chim. et Phys.* vi.

† Braconnot, *Annales de Chim. et Phys.* ix. 181.

Boil an ounce of powdered galls in 16 ounces of water down to 8, and strain; dissolve 2 ounces of alum in water, precipitate the alumina by carbonate of potasa, and, after edulcorating it, stir it into the decoction; the next day filter the mixture; wash the precipitate with warm water, till this will no longer blacken sulphate of iron; mix the washing with the filtered liquor, evaporate, and the gallic acid will be obtained in acicular crystals.*

1970. Gallic acid, when pure, is in whitish crystals, of a sour taste, and which exhale a peculiar smell when heated. It dissolves in about 24 parts of water at 60°, and in 3 parts at 212°. It is also soluble in alcohol and in ether. When repeatedly sublimed, this acid is altered and in part decomposed. It consists, according to Berzelius† of

| | |
|--------------------|--------|
| Hydrogen | 5,00 |
| Carbon | 56,64 |
| Oxygen | 38,36 |
| | <hr/> |
| | 100,00 |

These proportions give the number 63, as the representative of gallic acid.‡

1971. The combinations of pure gallic acid with metallic bases have scarcely been examined, and consequently we have no accurate chemical history of the *gallates*. Their solutions are all very prone to decomposition, and acquire a deep brown colour. This acid forms no precipitate in solutions of potassa or of soda, but when dropped into lime-water, baryta-water, or strontia-water, it occasions the separation of a difficultly soluble gallate of those earths. It also causes a precipitate in solutions of zirconia, glucina, and yttria.

1972. When an infusion of galls is added to certain metallic solutions, it forms precipitates composed of tannin, gallic acid, and the metallic oxide, and as these are often of different colours, the infusion is employed as a test for such metals. For the colours of the precipitates, see *Tables*.

1973. Of these compounds, the *tanno-gallate of iron* is of the most importance, as forming the basis of writing ink, and of black dyes.

When an infusion of galls is dropped into a solution of sulphate of iron, it produces a deep purple precipitate, which is a very long time in subsiding; it becomes black by exposure to air. In writing ink, this precipitate is retained in suspension by mucilage, and the following proportions appear the best which can be used.

| | |
|---------------------------------------|-----------------------------|
| Finely bruised galls, 3 ounces | Gum arabic, of each 1 ounce |
| Green vitriol (protosulphate of iron) | Vinegar, 1 quart |
| Logwood shavings. | |

Put these ingredients into a bottle, and agitate them occasionally during twelve or fourteen days; then allow the coarser parts to settle, and pour off the ink for use.

* Fiedler, Ure's Dictionary.

† *Annals of Philosophy*, vol. v.

| | | | |
|------------------------|---------|-------|---------|
| § Or, Carbon | 6 atoms | 36 | 57,14 |
| Oxygen | 3 | 24 | 38,10 |
| Hydrogen | 3 | 3 | 4,76 |
| | | <hr/> | <hr/> |
| | | 63 | 100. H. |

The tendency of ink to become mouldy is much diminished by keeping a few cloves in the ink bottle, or by dissolving in each pint of the ink about three grains of corrosive sublimate.

Colour re-
stored.

The colour of common writing ink is apt to fade, in consequence of the decomposition of its vegetable matter; and when thus illegible, it may often be restored by washing the writing with vinegar, and subsequently with infusion of galls. Acids also destroy its colouring matter, and those inks which resist their action contain some other colouring principle, usually finely powdered charcoal. Common writing ink is, for this reason, much improved by dissolving in the quantity above-mentioned about an ounce of *Indian Ink*, which is lamp-black made into a cake with isinglass.*

In dyeing black the stuff is first impregnated with a solution of the gall-nut, and afterwards the colour is brought out by the application of sulphate or acetate of iron.†

vi. BENZOIC ACID.

1974. Benzoic acid may be obtained by sublimation from *benzoin*, which is a resinous exudation from the *Styrax benzoe* of Sumatra; it also exists in the *Balsam of Peru* and of *Tolu*.‡ If these substances are heated in a crucible, with a cone of paper attached to its mouth, the acid condenses in it, in fine acicular crystals which were formerly called *flowers of benzoin*. A good process for procuring this acid is that recommended by Mr Hatchett which consists in digesting benzoin in sulphuric acid, when it affords a copious sublimate of pure benzoic acid.§ It may also be obtained by boiling a pound and a half of powdered benzoin with 4 ounces of quicklime, in 6 or 8 quarts of water. When cold the clear liquor is decanted, and the residuum again boiled in half the former quantity of water. The liquors thus obtained are boiled down to half their bulk, filtered, and mixed with muriatic acid, as long as it occasions a precipitate, from which the liquor is poured off, and when dry it is put into an earthen vessel, placed in a sand heat, and sublimed into paper cones.||

How obtain-
ed.

Characters.

1975. Benzoic acid, when it has been thus sublimed, is in the form of soft feathery crystals, and of an acrid and slightly

* See Dr Macculloch on Indelible Ink, &c. Brewster's *Jour.* i. 318, and *Bost. Jour.* ii. 344.

† Upon these subjects much valuable information will be found in Lewis's *Philosophical Commerce of the Arts*, and in Aikin's *Dictionary*.

‡ In the *Philos. Trans.* for 1817 Mr Brande has described the properties of a species of galls from China, which furnish very pure gallic acid, and which, could they be abundantly obtained, would certainly prove a valuable substitute for common galls, in many of the processes in which they are employed.

§ M. Vogel has detected it in crystals in the Tonquin bean. It is found in considerable quantity in the urine of the cow and other herbivorous animals.

|| Additional Experiments on Tannin, *Phil. Trans.* 1808.

|| In the tenth volume of Nicholson's *Journal*, Mr Brande has detailed several experiments on benzoin, and has shown the relative quantity of acid afforded by the several processes which have been recommended for obtaining it.

sour taste, soluble in about 30 parts of boiling water, and very sparingly soluble in cold water. It is much more soluble in alcohol, and this solution easily furnishes it in prismatic crystals.

1976. Berzelius's analysis gives the following as the components of this acid :

| | | | |
|--------------------|-----------|----|--------------|
| Hydrogen | 6 atoms = | 6 | Composition, |
| Carbon | 15 " = | 90 | |
| Oxygen | 3 " = | 24 | |

Equivalent of benzoic acid 120

1977. The compounds which this acid forms with alkaline and earthy bases are called *benzoates* ; they have been described in the *Philosophical Magazine*, vol. xl. and *Ann. de Chim.* vol. ix.*

Besides the vegetable acids which have now been described, Other acids: there are a few others of considerably inferior interest and importance ; namely, the

1978. *Moroxylic acid*, discovered by Klaproth, in the bark Moroxylic: of the *morus alba*, or *white mulberry*.† An exudation was observed upon this bark, which proved to be a compound of a peculiar acid and lime, or a *moroxylate of lime* ; its solution was decomposed by acetate of lead, and the *moroxylate of lead* thus obtained decomposed by dilute sulphuric acid, furnished a solution of moroxylic acid, which gave acicular crystals on evaporation. This acid has the taste of succinic acid ; it is soluble in water and alcohol, and does not, like some of its salts, form precipitates in metallic solutions. The quantity of this acid examined by Klaproth, was so small as to leave some doubt respecting its distinct nature.

1979. *Boletic acid* was obtained by Braconnot from the *boletus pseudoignarius*‡ by cautiously evaporating its expressed juice Boletic, to the thickness of sirup, digesting it in alcohol, dissolving the residue in water, and adding nitrate of lead to the aqueous solution ; the precipitate washed and diffused through water, was decomposed by sulphuretted hydrogen ; the liquor was then filtered and evaporated till it formed crystals, which were purified by solution in alcohol and evaporation. These crystals are boletic acid ; they are prismatic, and require 180 parts of water at 68°, and 45 of alcohol for their solution, which reddens blues and precipitates nitrate of lead, and the salts containing the peroxide, but not those of the protoxide of iron. This acid sublimes with little alteration, when heated. Braconnot has examined the *boletates of ammonia, potassa, lime, and baryta*, but his researches have not as yet been confirmed by any other chemist.§

1980. *Fungic acid* was procured by the same chemist from Fungic, the *boletus juglandis*, and some other fungi ; it is deliquescent and uncrystallizable.||

* See also Henry, ii. 220. † Nicholson's Journal, vii. ‡ Ann. de Chim. lxxx.
§ Thomson's System, 6th edit. ii. 137. || Ann. de Chim. lxxxvii.

Kinic.

1981. *Kinic acid** was discovered by Vauquelin, in *Cinchona*. When a strong cold infusion of this bark is set aside, crystals of *kinate of lime* are sparingly deposited by it, which may be decomposed by oxalic acid. The kinic acid is crystallizable, sour, and bitter: the *kinates* are for the most part soluble salts: it is chiefly distinguished by forming no precipitate in solutions of lead and silver.†

1982. M. Braconnot has given the term *Ellagic acid* (from the word *galle* reversed) to an acid body which he has detected along with gallic acid, in infusion of galls, but its characters have been but imperfectly ascertained.

Zumic.

1983. *Zumic acid* was discovered by the same chemist in vegetable substances, which have undergone acetous fermentation.‡

1984. M. M. Bussy and Lecanu have obtained three new fatty acids from castor oil, one called *ricinic acid*, is fusible at 72° F.; another termed *elaiodic acid*, is fluid below 32° F.; and the third or *margaritic acid*, crystallizes in fine scales, and is not fusible below 264° F.

Pectic acid.

1985. *Pectic Acid*.—M. H. Braconnot has given the name of *pectic acid*§ to a principle found by him in several plants which has the property of being coagulated by alcohol, metallic solutions, the acids, &c. It appears to be the same substance previously discovered by Professor Torrey in the Tuckahoe, *Sclerotium giganteum*,|| a fungus common in the sandy barrens of the Southern states, and to which he gave the name *Sclerotin*. It is readily soluble in a solution of caustic potassa, and this solution is gelatinized by almost every known body.

How obtained.

1986. M. Braconnot's process for obtaining this substance is as follows. If roots containing starch be operated upon, such as those of cellery and carrot, they are to be reduced to pulp by rasping, the juice expressed, the residue boiled in water, slightly acidified with muriatic acid, then washed, and afterwards heated with a very dilute solution of potassa or soda. A thick mucilaginous liquid results, slightly alkaline, from which muriatic acid separates the acid in the form of an abundant jelly, which should then be well washed.

Union with potassa.

1987. It forms a very soluble salt with potassa, which may be obtained in the state of a transparent jelly, by adding weak alcohol, which removes the excess of alkali and colouring matter if there be any present. This jelly washed on a cloth with alcoholized water, pressed and dried, is a neutral compound, which swells and dissolves in water, and leaves upon evaporation a transparent mass, resembling gum arabic. Its taste is insipid. Placed upon a plate of red hot iron it swells excessively, leaving a deep brown residue soluble in water, and having

Properties.

* Mr Brande proposes the term *cinchonic acid* as preferable. *Man. of Phar.* 64.

† *Ann. de Chim.* lix.

‡ Thomson's *System*, vol. ii. p. 189.

§ From *πικτικόν* coagulum.—*Ann. de Chim.* xxviii. 173, and *Boston Jour.* iii. 132.

|| Dr Torrey's analysis of the Tuckahoe was published in the *N. Y. Med. Rep.* 1820.

the character of ulmin united to potassa. Exposed to the flame of a taper, it burns, producing delicate filaments which project from the mass like vermicelli. These filaments fuse into globules of sub-carbonate of potassa.

This salt has the remarkable effect of communicating to large masses of sugar and water the property of gelatinizing. M. Braconnot in this way prepared aromatised jellies, perfectly transparent and colourless and very agreeable to the taste and eye.

1988. This acid forms with ammonia a soluble compound having similar properties to the foregoing. Unites with ammonia.

SECTION XVII. Of the Parts of Plants.

1989. In the preceding Sections the principal proximate components of vegetables have been described, and the composition of some of their detached parts has been adverted to; such of these as have not been previously noticed and as have been examined with any degree of precision, remain to be described in this Section under the heads of

- Roots.
Barks.
Woods.
Leaves.
Flowers.

Seeds.
Fruits.
Bulbs.
Lichens.
Fungi.

i. ROOTS.

1990. *a. Ipecacuanha*.—This root is the produce of the *Callicocca Ipecacuanha*.* Ipecacuanha. It has been examined by M. M. Pelle-
tier and Majendie, and an account of their researches is publish-
ed by M. Robiquet, in the *Annales de Chimie et Phys.* iv.
172. 100 parts of this root deprived of the woody fibre which
traverses its centre afforded

| | | | |
|------------------------|----|--------------------------|-------|
| Fatty matter | 2 | Woody fibre | 48 |
| Emetine | 14 | A trace of wax | |
| Gum | 16 | Loss | 2 |
| Starch | 18 | | <hr/> |
| | | | 100 |

The means of separating the emetic principle have already been described.

1991. *b. Valerian*, the root of the *Valeriana officinalis*, Valerian.
has been examined by Trommsdorf.† The recent root loses
about three-fourths its weight in drying. It affords, when dis-
tilled with water, an aromatic volatile oil; it also contains
starch, gum, resin, and extractive.

1992. *c. Turmeric* is the root of the *Curcuma longa*, a Turmeric.
plant cultivated in the East Indies, and used as a condiment,

* Linnæan Trans. vi.

† Ann. de Chimie, lxx.

especially in *Curry powder*. Digested in water or alcohol, it furnishes a large proportion of yellow colouring matter, which would be very useful to the dyer, could it be rendered permanent. Most of the acids render it paler, and the alkalies change it to a deep brick-red; hence its use as a test of the presence of alkaline matter. It is also reddened by boracic acid, and by muriatic acid gas.

Madder. 1993. *d. Madder* is the root of the *Rubia Tinctorum*, and is an article of great importance in dyeing; it grows wild in most parts of the south of Europe, and is largely cultivated in some parts of Holland and the Levant; its red colour is apt to be injured by drying, a process requiring much caution. Good madder has a strong and peculiar smell; it exhibits, when cut, a cortical and a woody part of a red colour, intermixed in the former with yellow spots. The red portion is most soluble.*

Rhubarb. 1994. *e. Rhubarb* is the root of the *Rheum palmatum*, largely cultivated in the northern parts of China; its colour is brown, with streaks of red and white. The following are the component parts, separable from the finest kinds of Turkey rhubarb.†

| | | | |
|-------------------------------|------|-----------------------------|------|
| Water | 8,2 | Phosphate of lime | 2,0 |
| Gum | 31,0 | Malate of lime | 6,5 |
| Resin | 10,0 | Woody fibre. | 16,3 |
| Extract, tan, and gallic acid | 26,0 | | |

Rheine. 1995. M. Vaudin, by treating one part of rhubarb with eight parts of nitric acid, with a gentle heat, and then reducing it to the consistence of a sirup and diluting it with water, observed that a peculiar substance was precipitated, which he has called *Rheine*. It is of a yellowish orange colour, devoid of any peculiar smell; its taste is slightly bitter, and it is almost entirely soluble in alcohol and ether; these solutions become yellow by acids, and of a rose colour by alkalies.‡

Rhubarbarine is the name employed by Pfaff to designate the principle in which the purgative property of the rhubarb resides. M. Nani of Milan regards the active principle of this plant as a vegetable alkali.§ From experiments on this substance Mr Carpenter infers that it is not the active principle of rhubarb.||

Althein. 1996. *Althein* was obtained by M. Bacon of Caén from the root of the *athea officinalis* by the following process.

Prepare a cold watery extract of marshmallow root, treat it with boiling alcohol, which dissolves acidulous malate of althein, oil, &c. Mix all the spirituous decoctions, which become turbid as they cool, pour off the clear solution, treat the crystalline deposit with water, filter the solution, and evaporate it with a gentle heat to the consistence of a sirup, and set it aside to crystallize. The crystals obtained are to be washed with a small quantity of water, and dried upon paper.

* Aikin's Dictionary, Art. Dyeing. Bethollet, *Elem. de Teinture*, ii.

† Brande, *Quarterly Journal of Science and the Arts*, x. 291.

‡ *Jour. de Chim. Med.* ii. 286.

§ *Quart. Jour.* xvi. 172.

|| See a paper by Mr Carpenter in *Amer. Jour. of Sci.* xiv. 33.

The crystals appear to the unassisted eye in the form of grains, needles, and feathers, and stars, but when examined with a glass they exhibit the hexaedral form. They are of a magnificent emerald green colour, inodorous and unaltered by exposure to the air; they redden litmus paper, are soluble in water, but insoluble in alcohol. The aqueous solution of these crystals, treated in the cold with magnesia, and filtered, restores the colour of litmus which has been reddened by an acid, and renders sirup of violets green: by evaporation the althein is obtained separate from the malic acid.*

1997. *Dalhine*.—This substance was extracted by Lagen from the roots of the *Dalhia*. It is white, and pulverulent, having most analogy with starch and inulin.†

1998. *Liquorice*, the root of the *Glycyrrhiza glabra*, has been examined by M. Robiquet, who found in it the following substances.‡

- | | |
|---|------------------------------------|
| i. Starch. | v. An acrid oil. |
| ii. Gluten. | v.i A crystallizable substance re- |
| iii. Liquorice sugar. | sembling asparagin. |
| iv. Phosphate and malate of lime and magnesia. | vii. Woody fibre. |

The sugar is soluble in water and in alcohol, but not convertible into alcohol by fermentation; nor into oxalic acid by the action of nitric acid.

1999. *Jalap*, the root of the *Convolvulus Jalappa*, is employed in medicine as a cathartic. It is imported from South America. Its activity is generally regarded as chiefly resident in its resin. The finest and densest jalap affords about 12 per cent. of resin, when digested in alcohol; water takes up about 30 or 35 per cent. of the remainder, and the residue appears to be inert woody fibre.

2000. *Gentian* is the root of the *Gentiana lutea*; according to Mr Henry§ it contains the following substances:

- i. A substance resembling bird-lime.
- ii. A resin combined with an oil, which gives to gentian its peculiar odour.
- iii. A bitter extractive principle.
- iv. Gum and colouring matter.
- v. Phosphate of lime.

ii. BARKS.

2001. *a. Cinchona*.—The varieties of Peruvian bark have been examined by M. M. Pelletier and Caventou.|| In the *cinchona lancifolia*, or *pale bark*, they found the following constituent parts:

- | | |
|---|--------------------|
| i. Cinchonia, combined with kinic acid. | iv. Tannin. |
| ii. Green fatty matter. | v. Kinate of lime. |
| iii. Red and yellow colouring matter. | vi. Gum. |
| | vii. Starch. |
| | viii. Lignin. |

* *Jour. de Chim. Med.* ii. and *Ann. Philos.* N. S. 7. 69. † *Ann. de Chim. et de Phys.* xxiv. 209.
‡ *Ann. de Chim.* lxx. § *Annals of Philosophy*, xvi. 89.
|| See also a paper by Mr Carpenter in *Amer. Jour.* ix. 363.

Cinchonia,
how obtain-
ed.

2002. *Cinchonia* may be obtained by the following process.

A pound of bruised bark is to be boiled in about a gallon of water, to which three drachms of sulphuric acid have been previously added. A similar decoction is to be repeated with about half the quantity of liquid, and so on till all the soluble matter is extracted. The decoctions are then to be mixed together and strained, and powdered hydrate of lime to be added, in proportion somewhat greater than is required to saturate the acid. From the precipitate (a mixture of cinchonia and sulphate of lime) repeated boilings for some minutes with alcohol, decanting the fluid while hot, separate the cinchonia, which may be obtained by distilling off the alcohol at a very gentle heat.*

Properties.

2003. *Cinchonia* thus obtained is white, translucent, crystalline, and soluble in 2500 times its weight of boiling water, but a considerable part separates on cooling. Its taste is bitter, though long in being developed, owing to its insolubility; but its acid solutions have a strong taste of Peruvian bark. It is neither fusible nor volatile at moderate temperatures. It is very soluble in alcohol and ether, and sparingly so in fixed and volatile oils.

2004. *Cinchonia* restores the colour of litmus, which has been reddened by an acid; unites with all the acids; and, with the greater number, forms compounds which are perfectly neutral. The sulphate is constituted of 11,27 acid, and 88,73 base. It is very soluble and has an intensely bitter taste. The muriate is still more soluble in water than the sulphate; dissolves in alcohol; and crystallizes in delicate prisms. The nitrate is not crystallizable. The oxalate, tartrate, and gallate of cinchonia are insoluble. Hence it is that infusion of galls precipitates the decoction of cinchonia.† H. 2. 310.

Quinia.

2005. In the *yellow bark* (*cinchonia cordifolia*) M. M. Pelletier and Caventou discovered a salifiable base, which is termed *Quinia*.‡ It may be prepared by a process similar to that above described for the preparation of cinchonia. When dried it is a white porous mass, incapable of crystallization from its alcoholic solution. In water it is as insoluble as cinchonia but is much more bitter; it is, however, very soluble in ether. *Quinia* is distinguished from cinchonia, by its smaller capacity of saturation, 360 parts of it being required to neutralize the same quantity of acid as 315 of cinchonia.

Sulphate.

2006. *Sulphate of Quinia*.—This salt is considered as the most active form of the salifiable principle of bark§ and may be prepared by the following process of M. Henry.

The bark is reduced to powder, and boiled twice for about a quarter or half an hour in 14 or 15 pints of water, two ounces of sulphuric acid being added to it each time. The decoctions contain the sulphate of quinia, are of a reddish colour, which gradually acquire a yellow tint, and have a very strong bitter

* Brande's Pharmacy, 61.

† See *Ann de Chim. et Phys.* xv. 289, 337; xvii. 273, 316; and *Ann. of Philos.* N. S. ii. 316. || H. 2.

‡ For a process for determining whether bark contains quinia see *Ann. Philos.* N. S. xii. 464.

§ Mr R. Phillips has given a paper "on the means of ascertaining the purity of Sulphate of Quinia" in *Ann. Philos.* N. S. xiv. iii.

|| Nitrate of *Cinchonia* appears to be uncrystallizable. Gallic, oxalic, and tartaric acids form difficultly soluble salts with cinchonia; the precipitate occasioned by dropping tincture of galls into infusion of pale bark is a *gallate of Cinchonia*.

taste. They are to be filtered through a linen cloth, and about half a pound of pulverized quicklime is to be gradually added to the solution: the sulphate of quinia is decomposed, the alkali being precipitated along with the sulphate of lime. This is digested repeatedly in rectified alcohol, till it no longer imparts any bitter taste to this fluid; the alcoholic solutions are then evaporated till a very bitter, brown viscid substance is obtained, which becomes brittle as it cools. This is the quinia separated from almost all the other ingredients of the bark; and by digesting it in dilute sulphuric acid, a solution of the sulphate of quinia is obtained, which crystallizes on evaporation.

Two lbs of bark yield from 5 to 6 drachms of the sulphate. It consists of 100 quinia + 10,9 acid.

2007. *Acetate of Quinia* forms bundles of flat acicular crystals, while the corresponding salt of cinchonia crystallizes in small tables. The *gallate*, *oxalate* and *tartrate of quinia*, are nearly insoluble, but quinia is very soluble in sulphuric ether. Acetate.

2008. In the *red bark* (*cinchona oblongifolia*) the two salifiable bases above described are found united.*

2009. *b.* The bark of the *horse chestnut* (*Æsculus hippocastanum*,) has been partially examined by M. Henry.† It appears to contain scarcely any resin; water and diluted alcohol dissolve nearly the whole of its soluble contents, which are chiefly extractive and mucilage. Tincture of galls does not render its infusion turbid, it does not therefore probably contain the peculiar substances discovered in Peruvian bark.

iii. Woods.

2010. *a. Brazil Wood* is the produce of the *Cæsalpina* Brazil wood.
crista, growing in Brazil, in the Isle of France, Japan, and other countries: the wood is hard and heavy, and though pale when recent, it acquires a deep red colour by exposure. Digested in water it affords a fine red infusion, of a sweetish flavour; the residue, which appears nearly black, imparts much of its colour to alkaline liquors. With alcohol it gives a deep red tincture: alkalies and soap convert its red colour to a fine purple, hence paper tinged with Brazil wood is sometimes used as a test for alkalies; acids render it yellow; alum produces a fine crimson lake with infusion of Brazil wood; muriate of tin forms with it a crimson precipitate, bordering on purple; the salts of iron give a dingy purple colour. Sulphuretted hydrogen destroys the colour of infusion of brazil wood, but it reappears on expelling the gas.‡

* *Quarterly Journal of Science and the Arts*, x, 388.

† *Cascarilla*, the bark of the *Croton Eleutheria* contains, according to Trommsdorff.—*Annales de Chimie*, xxii.

| | Parts. |
|-------------------------------|--------|
| Mucilage and bitter principle | 864 |
| Resin | 688 |
| Volatile oil | 72 |
| Water | 48 |
| Woody fibre | 3024 |

4696

‡ Chevreuil, *Ann. de Chim.* lxi.

Sandal wood. 2011. *b. Red Sandal*, or *Saunders*, is the wood of the *Pterocarpus santalinus*, a native of several parts of India. Its deep red colouring matter is insoluble in water, but readily soluble in alcohol; it is chiefly employed for colouring a few pharmaceutical tinctures. The insolubility of its colouring principle in water furnishes a ready mode of distinguishing between it and Brazil wood; and its solubility in alcohol renders it probable that it is of a resinous nature.

Logwood. 2012. *c. Logwood*, the produce of the *Hæmatoxylon campechianum*, has already been noticed as containing a peculiar colouring principle. (1827.) It imparts a fine purple or crimson colour to pure water, but its tint is altered by the slightest metallic impregnation; alkalies deepen it, and acids render it paler; alum forms with it a violet-coloured lake; sulphate of iron renders the infusion of logwood deep purple, or nearly black; sulphate of copper and acetate of lead throw down brown and purple precipitates; and muriate of tin precipitates the whole of the colouring matter, in the form of a purple compound. The colours which logwood produces are for the most part very perishable.*

iv. LEAVES.

Senna. 2013. *a. Senna*.—According to Lagranget the leaves of the *Cassia senna* are characterized by containing a peculiar extractive principle, which, by long boiling, passes into a resinous substance, in consequence of absorbing oxygen; they also contain a resin which resists the action of water, and is soluble in alcohol; the whole of the soluble matter amounts to about one-third the weight of the senna. In the *London Medical Repository*, vol. xv. 169, the effects of the various re-agents on infusion of senna are detailed by Mr Batley.

Nightshade. 2014. *b. Nightshade*.—The leaves of the *Atropa Belladonna* contain according to Vauquelin†

- i. Vegetable albumen.
- ii. A bitter narcotic principle.
- iii. Nitrate, muriate, sulphate, binoxalate, and acetate of potassa.

Dr Brandes has announced the existence of a new vegetable alkali in this plant, which he calls *atropia*. It forms brilliant acicular crystals, tasteless, and difficultly soluble in water and alcohol. It affords distinct salts with the acids; the *Sulphate of Atropia* consists of

| | |
|--------------------------|-------|
| Sulphuric acid | 36,52 |
| Atropia | 38,93 |
| Water | 24,55 |

100,00

Henbane. 2015. *c. Hyoscyamus Niger*, or *Henbane*.—In the leaves of this plant Dr Brandes has also ascertained the presence of a

* Bancroft on Permanent Colours, ii. 338. Chevreuil, *Ann. de Chim.* lxxi. 254.

† *Ann. de Chim.* xxvi.

‡ *Ann. de Chim.* lxxii.

peculiar and highly poisonous salifiable base which he calls *hyosciana*. With the acids it forms characteristic salts; it crystallizes in long prisms.

2016. *Lupulin* was discovered by Dr Ives* and M. M. Payen and Chevalier, about the same time, in the leaves of the *Humulus Lupulus* or common hop. It is extremely bitter, of a yellow colour, and has an aromatic odour. It is the principle on which the characteristic properties of the hop depend.

V. FLOWERS.

2017. The colouring matter of most flowers is extremely fugitive, and is generally much changed by mere exsiccation. They usually communicate their colour to water; the infusion of blue flowers is generally reddened by acids, and changed to green or yellow by alkalies; that of yellow flowers is made paler by acids, and alkalies render it brown; the red infusion of many flowers is exalted in tint by acids, and changed to purple, and in some instances, to green, by alkalies.

Colouring
matter of
flowers.

It is probable that one and the same principle gives colour to several of the blue and red flowers, but that the presence of acid in the latter produces the red; the petals of the red rose, triturated with a little carbonate of lime and water, give a blue liquor; alkalies render it green, and acids restore the red.

2018. A colouring matter analogous to that of the violet, exists in the petals of red clover, in the red tips of those of the common daisy, of the blue hyacinth, the holly-hock, lavender, in the inner leaves of the artichoke, and in numerous other flowers; reddened by an acid, it colours the skin of several plums, and the petals of the scarlet geranium and pomegranate. Some flowers which are red, become blue by merely bruising them; this is also the case with the colouring matter of red cabbage leaves, and of the rind of the long radish. Mr Smithson has suggested that the reddening acid is in these cases the carbonic, which escapes on the rupture of the vessels which enclose it.

2019. The petals of the common *corn-poppy*, rubbed upon paper, give a purple stain, little altered by ammonia or carbonate of soda, but made green by caustic potassa. The infusion of poppy-petals in very dilute muriatic acid, is florid red; chalk added, renders it of the colour of port wine; carbonate of soda in excess gives the same colour, but excess of potassa changes it to green and yellow. The expressed juice of the black mulberry possesses nearly the same properties.†

2020. The flowers of the *carthamus tinctorius*, or *safflower*, cultivated chiefly in Spain and the Levant, contain a yellow colouring matter, easily soluble in water, and a red, soluble in alcohol and weak alkaline liquors; the latter only is employed.

* *American Journal of Science*, ii.

† Smithson, *Phil. Trans.* 1812. 119.

Rouge.

Rouge is the red colouring matter of the carthamus, obtained by digesting the washed flowers in solution of carbonate of soda, and adding lemon juice, which throws it down in the form of a fine powder, which is dried and mixed with a portion of powdered tale; carthamus is also used for dyeing silk. The details of the analysis of carthamus will be found in the *Essays of Dufour and Marchais*.*

Pollenin.

2021. *Pollenin* is prepared from the polen of tulips, and was discovered by Dr John. It is distinguished by its insolubility in all those agents which are usually employed to effect the solution of other vegetable products, and is highly inflammable, burning rapidly with a large flame. When exposed to the air it soon passes to a state of putrefaction; and by destructive distillation, ammonia is disengaged, along with some of the usual products that arise from the decomposition of animal matter.†

vi. SEEDS.

2022. Starch is an essential component of the greater number of seeds, and it is generally united in them with a variable portion of gluten, and often of fixed and of volatile oil. The component parts of wheat-flower, and of several esculent grains, have already been stated (1803,) and a variety of curious details respecting them will be found in EINHOFF's *Papers*, in GEHLEN's *Journal*.

Sir H. Davy has also examined a number of seeds with a view to determine their relative nutritive powers: for the results of his experiments see *Agricultural Chemistry*, 4to. 131.

Almonds.

2023. *Almonds*, the seeds of the *amygdalus communis*, consist of an albuminous substance and oil; the latter may be obtained by expression, five pounds yielding about one pound of cold drawn oil, and about a pound and a half when aided by heat. The bitter almond affords by pressure an oil analogous to that from the former; but if the expressed cake be distilled with water, a portion of volatile oil eminently poisonous, and smelling strongly of the almond, is obtained; this oil is used as a flavouring material by confectioners, and by the manufacturers of noyau.‡

2024. The seeds of the *white lupine* (*lupinus albus*) contain, according to Fourcroy and Vauquelin§, gluten and a green acrid oil, with a considerable portion of phosphate of lime and magnesia, but no starch or sugar.

* *Ann. de Chim.* xlviii.

† *Chlorophylle* is a term which is applied to the green colouring matter of plants, and is obtained by subjecting the green parts, especially the leaves, to pressure along with water, treating the residue with alcohol, and evaporating the solution. It is purified from a brown colouring matter by warm water. It is soft, viscid, and of a fine green colour, soluble in sulphuric acid without being decomposed, and is precipitated by water and solutions of the alkalis. It is very soluble in alcohol and ether, but is sparingly dissolved by water.

‡ In the *Philosophical Transactions* for 1811, Mr Brodie has detailed a variety of experiments illustrative of its action as a poison, in which, as well as from its odour it appears identical nearly with hydrocyanic acid.

§ *Ann. du Muséum*, No. xxxvi.

2025. *Coffee*, the seed of the *Coffea Arabica* has been examined both in its raw and roasted state. From 64 parts of raw coffee,* Cadet obtained

| | |
|---|------|
| Gum | 8, |
| Resin and bitter extract | 2,0 |
| Gallic acid | 3,5 |
| Insoluble matter | 43,5 |
| Loss including a trace of albumen | 7,0 |

64.

Hermann has given the following comparative analysis of coffee from the Levant and from Martinique,† the results of which differ much from those of Cadet:

| | Levant. | Martinique. |
|--------------------------|------------|-------------|
| Resin | 74 | 68 |
| Extractive | 320 | 310 |
| Gum | 130 | 144 |
| Fibrous matter | 1335 | 1386 |
| Loss | 61 | 12 |
| | <hr/> 1920 | <hr/> 1920 |

When coffee is roasted it undergoes a peculiar change of composition attended by the formation of tan, and a volatile, fragrant, and aromatic principle; but in this state it has not been examined with any precision.

2026. *Cafeine* is a new principle which was discovered in coffee by Robiquet. It is white, volatile, and crystallizable, and is particularly distinguished by the large quantity of nitrogen which it contains, being greater than that in almost any other vegetable. According to Dumas and Pelletier, it consists of 27,14 oxygen, 4,81 hydrogen, 46,51 carbon, and 21,54 nitrogen. Cafeine.

2027. *Mustard*.—The seed of the *sinapis nigra* derives its acrimony from volatile oil; it also contains a tasteless fixed oil, albumen, gum, and traces of sulphur and earthy salts. Mustard.

2028. The seeds of the *lycopodium clavatum*, or common club moss have been analyzed by Bucholz.‡ From 1000 parts he obtained Lycopodium.

| | |
|-----------------------------|-----|
| Fixed oil | 60 |
| Sugar | 30 |
| Mucilage | 15 |
| Insoluble residue | 895 |

1000

This seed has the appearance of a fine yellow powder, which deflagrates when projected into the flame of a candle; it is used in theatres to imitate lightning; and the German apothecaries employ it to prevent the adhesion of pills.

2029. *Annotta* is the produce of the *bixa orellana*, a tree cultivated in various parts of America. When the capsules are ripe, the seeds are bruised and steeped for several weeks in water, until converted into a pulp, which is allowed to putrefy, Annotta.

* Ann. de Chim. lviii.

† Crell's Annales, ii.

‡ Gehlen's Journal, vi.

and being diffused through a fresh portion of water, is heated till a scum rises, which is successively removed as it forms, and being carefully dried, is made up into cakes, and wrapped in palm leaves for exportation.

Annotta is soluble in water and alcohol; the solutions have a disagreeable smell, and are of an orange colour; alkalies render it more soluble and increase its colour; alum and the acids separate it from its solutions in the form of a yellow sediment; it is used for dyeing silk and colouring cheese.

Citisin.

2030. *Citisin* was discovered by M. M. Payen and Chevalier in the seeds of the *Cytisus Laburnum*. Its colour is yellow, and it has a disagreeable taste; it is soluble in water, alcohol and ether. It is easily decomposed by heat, and the strong acids produce the same effect.

vii. FRUITS.

Their contents.

2031. The acid matter contained in fruits is either the tartaric, oxalic, citric, or malic; or a mixture of two or more of them; but the nature and proportion of the acid varies at different periods of their growth; gluten and starch are found in some fruits, and a gelatinizing substance, which has sometimes been regarded as identical with animal jelly, but which is probably a compound of gum and one or more vegetable acids.

Fruits contain sugar.

2032. Most of our common fruits also contain sugar, and it exists in all those the juice of which is susceptible of vinous fermentation. In some fruits the quantity of sugar is increased by mashing and exposure to air; this is remarkably the case with some of the rough-flavoured apples used for cider, the pulp of which becomes brown, and at the same time sweet by a few hours' exposure.

Colouring matter.

2033. The colouring matter of fruits seems in most cases to bear a strong resemblance to that of flowers. The red juice of the mulberry was found to exhibit the same characters as the colouring principle of the wild poppy; carbonated alkalies render it blue, but caustic potassa changes it to green and yellow: the juice of red currants, cherries, elder-berries, and privet-berries, and the skin of the buckthorn berry, appear to contain a similar colouring principle.

Sap green.

2034. The unripe berries of the buckthorn furnish a juice, which, when inspissated, is known under the name of *sap green*. It is soluble in water, and rendered yellow by carbonate of soda and caustic potassa; the acids redden it, and carbonate of lime restores it to green, which is therefore probably the proper colour of the substance.*

Elatarium.

2035. The fruit of the *wild cucumber* (*cucumis elaterium*) furnishes a very acrid juice, which deposits the powerful cathartic known under the name of *elaterium*. This substance

* Smithson, *Phil. Trans.* 1818, p. 116.

occurs in commerce in thin cakes, of a greenish colour and bitter taste ; it derives its cathartic power from a small portion of a very active principle, which Dr Paris has called *Elatin* :* from 10 grains of elaterium he obtained

| | | |
|------------------------|-----|-----------|
| Water | 0,4 | |
| Extractive | 2,6 | |
| Fecula | 2,8 | |
| Gluten | 0,5 | |
| Woody matter | 2,5 | |
| Elatin | } | 1,2 |
| Bitter principle | | |
| | | <hr/> 10. |

2036. *Zeine* was discovered by Prof. Gorham in the *Zea* Zeine.
Mays or indian corn. It may be procured by infusing the grain in water, filtering, and digesting the insoluble residue in alcohol, and evaporating to dryness. It is of a yellowish colour, insipid, soft and elastic.†

viii. BULBS.

2037. The *potato*, which is the bulbous root of the *solanum* Potato.
tuberosum, has been examined by Dr Pearson and by M. Einhoff ; from 100 parts, the latter chemist obtained

| | |
|--------------------------------|-------|
| Starchy matter | 22 |
| Albumen and mucilage | 5,4 |
| | <hr/> |
| | 27,4 |

The average quantity of nutritive matter contained in the potato, amounts to about one fourth its weight. When potatoes become sweet by exposure to frost, a portion of mucilage passes into the state of sugar, for Einhoff found the quantity of starch undiminished.

2038. *Garlic* or the bulbous root of the *allium sativum*, has Garlic.
been examined by Cadet.‡ It loses by drying about two-thirds of its weight ; its juice is viscid, and very slightly sour ; it yields coagulated albumen when heated, and when distilled with water furnishes an acrid oil having a strong odour of garlic.

2039. The bulb of the *Allium Ceba*, or *Onion*, has been analyzed by Fourcroy and Vauquelin.§ The juice of this root when exposed to a temperature of about 70°, forms a quantity of vinegar, and deposits a sediment having the characters of gluten combined with oil and sulphur. In the acetous solution is contained a substance having the properties of manna, and which is probably a product of the fermentation, for none could be detected in the recent juice.

2040. *Squill*, the bulbous root of the *Scilla maritima* contains, according to Vogel,|| a peculiar bitter principle, which he terms *Scillitin*, combined with gum, and a considerable portion Scillitin.
of tannin.

* Pharmacologia, 223, 3d edit.

† N. E. Journal of Medicine.

‡ Ann. de Chim. lxx.

§ Ann. de Chim. lxxv.

|| Ann de Chim. lxxxiv.

ix. LICHENS.

Archil.

2041. There are several lichens which abound in colouring matter; of these the most remarkable is the *Lichen rocella*, which grows in the South of France and in the Canary Islands, and which affords the beautiful but perishable blue called *litmus*, *archil*, or *turnsole*. The moss is dried, powdered, mixed with pearlsh and urine, and allowed to ferment, during which it becomes red, and then blue; in this state it is mixed with carbonate of potassa and chalk, and dried. It is used for dyeing silk and ribands, and by the chemist as a most delicate test of acids, which it indicates by passing from blue to red; the blue colour is restored by alkalis, which do not render it green. *Cudbear* appears to be a similar preparation of the *lichen tartareus*.*

Mr Smithson has thrown some doubt upon the use of alkalis in the precipitation of litmus, for he found its tincture produce no change on solutions of muriate of lime, nitrate of lead, muriate of platinum and oxalate of potassa; he at the same time suggests the idea of its being a compound of a vegetable principle with potassa.†

Iceland moss.

2042. The *Lichen Islandicus*, or *Iceland Moss* has been subjected to analysis by Berzelius.‡ He obtained from it the following substances:

| | | | |
|----------------------------------|-----|-----------------------------|-------|
| Sirup | 3,6 | Wax | 1,6 |
| Bi-tartrate of potassa | 1,9 | Gum | 3,7 |
| Tartrate of lime | | Colouring extract | 7,0 |
| Phosphate of lime | | Starch | 44,6 |
| Bitter principle | 3,0 | Insoluble starchy matter | 36,6 |
| | | | 102,0 |

x. FUNGI OR MUSHROOMS.

Fungic acid.

2043. M. Braconnot who has examined many fungi with minute attention, has given the name *fungin* to the insoluble spongy portion which they contain, and which in many respects resembles lignin: he has also detected in them two peculiar acids, which he terms *fungic acid* (1980) and *boletic acid* (1979); the method of extracting which has been above described. A peculiar fatty matter, or adipocere, has been found by Vauquelin and Braconnot, in several of the fungi; an albuminous substance, and salts, some of which are boletates and fungates, have also been detected in them, but the analyses are too abstruse, and the results too complicated, to be regarded as perfectly satisfactory.§

* Bancroft on Colours, i. 300.

† Phil. Trans. 1818, p. 112.

‡ Ann. de Chim. xc.

§ Ann. de Chim. lxxix. lxxxv, &c.

SECTION XVIII. *Phenomena and Products of Fermentation.*

2044. The term *fermentation* is employed to signify the spontaneous changes, which certain vegetable solutions undergo, placed under certain circumstances, and which terminate either in the production of an intoxicating liquor, or of vinegar; the former termination constituting *vinous*, the latter *acetous* fermentation. Fermentation.
Vinous and
acetous.

The principal substance concerned in vinous fermentation is sugar; and no vegetable juice can be made to undergo the process, which does not contain it in a very sensible quantity. In the production of beer, the sugar is derived from the malt; in that of wine, from the juice of the grape.

2045. In the manufacture of *beer*, the malt is ground and infused in the *mash-tun*, in rather more than its bulk of water, of the temperature of 160° or 180°. Here the mixture is stirred for a few hours; the liquor is then run off, and more water added, until the malt is exhausted. These infusions are called *wort*, and its principal contents are *saccharine matter*, *starch*, *mucilage*, and a small quantity of *gluten*. The strength of the wort is adjusted by its specific gravity, which is usually found by an instrument, not quite correctly called a *saccharometer*, since it is influenced by all the contents of the wort, and not by the sugar only.* Beer.
Wort:

The wort is next boiled with hops, amounting upon the average, to $\frac{1}{20}$ the weight of the malt, their use being to cover the sweetness of the liquor by their aromatic bitter, and to diminish its tendency to acidify. The liquor is then thrown into large, but very shallow, vessels, or *coolers*, where it is cooled to about 50°, as quickly as possible; it is then suffered to run into the *fermenting vat*, having been previously mixed with a proper quantity of *yeast*, which accelerates fermentation, apparently by virtue of the gluten which it contains.

In the fermenting vessel, the different substances held in solution in the liquor begin to act upon each other; an intestine motion ensues, the temperature of the liquor increases, carbonic acid escapes in large quantities; at length this evolution of gas ceases, the liquor becomes quiet and clear, and it has now lost much of its sweetness, has diminished in specific gravity, acquired a new flavour, and become intoxicating.

2046. The distillers prepare a liquor, called *wash*, for the express purpose of producing from it ardent spirits; instead of Wash.

* It is a brass instrument, of the shape shown in fig. 126, so adjusted in weight as to sink to the point marked 0°, in distilled water, at the temperature of 70°, and when immersed in a liquor of the same temperature, and of the specific gravity of 1,100, it is buoyed up to the mark 100, just above the bulb. The intermediate space is divided into 100 equal parts, and consequently will indicate intermediate degrees of specific gravity. This is the most useful form of the instrument, though not that in common use. The specific gravity of the wort for ale is usually about 1,090 to 1,100, and for table beer from 1,020 to 1,030. Pl. viii.

brewing this from pure malt, they chiefly employ raw grain, mixed with a small quantity only of malted grain; the water employed in the mash-tun is of a lower temperature than that requisite in brewing, and the mashing longer continued; by which it would appear that a part of the starch of the barley is rendered into a kind of saccharine matter. The wort is afterwards fermented with yeast.

Wine.

2047. *Wine* is principally procured from the juice of the grape, and some other saccharine and mucilaginous juices of fruits. The principal substances held in solution in grape juice are, *sugar, gum, gluten, and bi-tartrate of potassa*. It easily ferments spontaneously at temperatures between 60° and 80°, and the phenomena it gives rise to closely resemble those of the wort with yeast. After the operation, its specific gravity is much diminished, its flavour changed, and it has acquired intoxicating powers.*

2048. If a mixture of 1 part of sugar, 4 or 5 of water, and a little yeast, be placed in a due temperature, it also soon begins to ferment, and gives rise to the same products as wort or grape-juice; and, as the free admission of air is not necessary to vinous fermentation, its results may easily be examined by suffering the process to go on in the apparatus, fig 127, consisting of a matrice containing the fermenting mixture, with a bent tube issuing from it, and passing into an inverted jar standing in water.

Gaseous products of fermentation.

It will thus be found that the only gaseous product is carbonic acid; and consequently, that carbon and oxygen are the principles which the saccharine matter loses during the process.

2049. When any of the above-mentioned fermented liquors are distilled, they afford a *spirituous liquor*; that from wine is termed *brandy*; from the fermented juice of the sugar-cane we obtain *rum*; and from wash, *malt spirit*; and these spirituous liquors, by re-distillation, furnish *spirit of wine, ardent spirit, or alcohol*.

2050. The different fermented liquors furnish very different proportions of alcohol, and it has been sometimes supposed that it does not pre-exist to the amount in which it is obtained by distillation; but some experiments made by Prof. Brande upon the subject, in 1811 and 1813, and which are printed in the *Philosophical Transactions* for those years, tend to show that it is a real educt, and not formed by the action of heat upon the elements existing in the fermented liquor.†

Pl. vii.

* The vegetable extract existing in the recent or expressed juice of the grape, is considered by Dr Macculloch and M. Thenard as the proper fermentative principle. The last of these chemists supposes that this extract tends to excite fermentation in consequence of its having the power of abstracting, by means of its hydrogen and carbon, a portion of oxygen from the sugar of the must. In this way the divellent affinities of the ingredients of the sugar are brought into action. A part of its oxygen and carbon is evolved in a gaseous form, while its hydrogen and the remaining oxygen and carbon are converted into alcohol — Brewster's *Jour.* 1, 164.

† For the proportion of alcohol existing in several kinds of wine and other liquors, see Henderson's table in Brewster's *Jour.* vol. 1, 166.

2051. *Alcohol*.—The principle upon which the intoxicating properties of fermented liquors depend, and which exists in ardent spirits, is in its purest form called *alcohol*. It may be obtained by distilling the *rectified spirit of wine* of commerce, with one-fourth of its weight of dry and warm carbonate of potassa; about three-fourths may be drawn over.* There are other substances which may be used as substitutes for the carbonate, especially chloride of calcium.

2052. It has been found also that spirit of wine of sp. gr. 867 when inclosed in a bladder, and exposed for some time to the air, is converted into alcohol of sp. gr. 0,817, the water only escaping through the coats of the bladder.†

2053. Alcohol obtained by slow and careful distillation, is a limpid, colourless liquid, of an agreeable smell, and a strong pungent flavour. Its specific gravity varies with its purity; the purest obtained by rectification over chloride of calcium being 791; as it usually occurs it is ,820 at 60°. If rendered as pure as possible by simple distillation, it can scarcely be obtained of a lower specific gravity than ,825, at 60°.

2054. Mr Hutton is said to have succeeded in freezing alcohol, but the fact is regarded as doubtful, as the means by which he effected its congelation were never disclosed. Mr Walker exposed it to a temperature of—91 but no congelation took place. Even when diluted with an equal weight of water, it requires a cold of 6° below 0 to congeal it. When of a specific gravity of ,825, it boils at the temperature of 176°, the barometrical pressure being 30 inches. In the vacuum of an air-pump it boils at common temperatures. The specific gravity of the vapour of alcohol, compared with atmospheric air, is 4,613.‡

2055. Alcohol may be mixed in all proportions, with water, and the specific gravity of the mixture is greater than the mean of the two liquids, in consequence of a diminution of bulk that occurs on mixture, as may be shown by the following experiment:

Fig. 128 represents a tube with two bulbs, communicating with each other, the upper one being supplied with a well-ground glass stopper. Fill the tube and lower bulb with water, pour alcohol slowly into the upper bulb, and when full put in the stopper. The vessel will now be completely filled, the alcohol lying upon the water; if it be inverted, the alcohol and water will slowly mix and the condensation that ensues will be indicated by the empty space in the tube. A considerable rise of temperature takes place in this experiment, in consequence of the condensation.

2056. The strength of such spirituous liquors as consist of little else than water and alcohol, is of course ascertained by their specific gravity; and for the purpose of levying duties upon them, this is ascertained by the hydrometer; an instrument constructed on the same principle as that described at page 535 (*note*.) But the only correct mode of ascertaining the specific gravity of liquids, is by weighing them in a deli-

Alcohol.

Effect of cold.

Condensation of alcohol and water.

Exp.

Pl. viii.

Strength, how ascertained.

* According to M. Hensmans it is best to add a little caustic potassa or soda. *Bull. Univ. E. yiii.* 289.

† *Quart. Jour.* viii. 381, and Henderson's *History of wine*, Lond. 1824.

‡ Gay-Lussac, *Annales de Chimie et Phys.*

cate balance against an equal volume of pure water, of a similar temperature.*

2057. There are other methods of judging of the strength of spirituous liquors, which, though useful, are not accurate, such as the taste, the size and appearance of the bubbles when shaken, the sinking or floating of olive oil in it, and the appearances it exhibits when burned; if it burns away perfectly to dryness, and inflames gunpowder or a piece of cotton immersed in it, it is considered as alcohol: the different spirituous liquors leave variable proportions of water when thus burned in a graduated vessel.†

Combustion
of alcohol.

2058. Alcohol is extremely inflammable, and burns with a pale blue flame, scarcely visible in bright day-light. It occasions no fuliginous deposition upon substances held over it, and the products of its combustion are carbonic acid and water, the weight of the water considerably exceeding that of the alcohol consumed. According to Saussure, jun. 100 parts of alcohol afford, when burned, 136 parts of water. the production of which may be shown by substituting the flame of alcohol for that of hydrogen, in the apparatus described in the first of the work, under the Article WATER (389), and if the tube at its extremity be turned down into a glass jar, it will be found that a current of carbonic acid passes out of it, which may be rendered evident by lime water.

Pl. 4, fig. 92.

There are some substances which communicate colour to the flame of alcohol; from boracic acid it acquires a greenish yellow tint; nitre and the soluble salts of baryta cause it to burn yellow, and those of strontia give it a beautiful rose colour; cupreous salts impart a fine green tinge.

2059. Alcohol dissolves pure soda and potassa, but it does not act upon their carbonates: consequently, if the latter be mixed with alcohol containing water, the liquor separates into two portions, the upper being alcohol deprived to a considerable extent, of water, and the lower the aqueous solution of the carbonate. The alcoholic solution of caustic potassa was known in old pharmacy under the name of Van Helmont's *Tincture of Tartar*. Its use in purifying potassa has already been stated

Tincture of
Tartar.

* In the *Philosophical Transactions* for 1794, Mr Gilpin has given a copious and valuable series of tables of the specific gravity of mixtures of alcohol and water, and of the condensation that ensues, with several other particulars. These are extremely useful, as enabling us to ascertain, without difficulty, the relative quantity of alcohol contained in any mixture of known specific gravity.

† There is the greatest difficulty in ascertaining what is meant by the term *proof spirit*. Dr Thomson, quoting the Act of Parliament of 1762 (*System*, ii. 319,) states, that at the temperature of 60°, the specific gravity of proof spirit should be 0.916; and he also observes, that *proof spirit* usually means a mixture of equal bulks, of alcohol and water; but the specific gravity of such a mixture will, of course, depend upon that of the standard alcohol, which is not specified. It appears from Gilpin's *Tables*, that spirit of the specific gravity .916 at 60°, consists by weight of 100 parts of alcohol, specific gravity .825, at 60°, and 15 of water; and, by measure, of 100 parts of the same alcohol, and 61.87 of water. From the *Tables* of Lowitz, quoted by Dr Thomson, from Crell's *Annals* (1798, i. 202.) we learn that equal weights of alcohol, specific gravity .796, at 60°, (and which may be regarded as pure alcohol,) and water, have a specific gravity of .917, which is very near legal proof, and which, according to Gilpin's *Tables*, contains 62.8 parts per cent. of his alcohol, by measure.

(960); if it be long kept it deposits small crystals of carbonate of potassa, and becomes nearly black, from the decomposition of a portion of alcohol; the greater number of sulphates are insoluble in this menstruum, but it dissolves many of the muriates and nitrates. It also dissolves the greater number of the acids. It absorbs many gaseous bodies. It dissolves the vegetable acids, the volatile oils, the resins, tan, and extractive matter, and many of the soaps; the greater number of the fixed oils are taken up by it in small quantities only, but some dissolve largely.*

2060. When the vapour of alcohol is passed through a red-hot copper tube, it is decomposed, a portion of charcoal is deposited, and a large quantity of carburetted hydrogen gas is evolved. Decomposition.

2061. The composition of alcohol was investigated by Saussure and Gay-Lussac by passing the alcohol through a red-hot porcelain tube, terminating in a glass tube six feet long and surrounded by ice; all the products were carefully collected and weighed. The result of this analysis was, that 100 parts of pure alcohol consist of

| | |
|--------------------|-------|
| Hydrogen | 13,50 |
| Carbon | 51,98 |
| Oxygen | 34,32 |

Composition.

 100,00†

These numbers approach to 3 proportionals of hydrogen = 3; 2 of carbon, = 12; and 1 of oxygen, = 8.

Or it may be regarded as composed of 1 vol. carburetted hydrogen and 1 vol. of the vapour of water: the two volumes being condensed into 1, the specific gravity of the vapour of alcohol, compared with common air, will be 1,599, or, according to Gay-Lussac, 1,613.

2062. When alcohol is submitted to distillation, with certain acids, a peculiar compound is formed, called *ether*, the different ethers being distinguished by the name of the acid employed in their preparation. Ether.

a. SULPHURIC ETHER.

2063. *Sulphuric Ether* is the most important of these compounds; it is prepared as follows: Preparation.

Equal weights of alcohol and sulphuric acid are carefully mixed and introduced into a glass retort placed in a sand-bath, to which is adapted a capacious tubulated glass globe, connected with a receiver, as represented in fig. 100. Pl. 4. Raise the mixture in the retort to its boiling point as rapidly as possible, and, keeping the receiver cool by water or ice, continue the distillation, till opaque vapours appear in the retort; then remove the receiver, and agitate its contents with a little quick-lime; after which pour off the clear liquor, and re-distil

* It may be remarked that many errors exist in the published estimates, of the solubility of substances in alcohol, arising from the existence of water either in the solvent or substance dissolved.

† The recent analysis of M. M. Dumas and Boullay is in accordance with the above. See *Quart. Jour. N. S.* v. 222.

to the amount of three-fourths its original quantity with the same precautions as before. The ether may be further purified by distilling it off chloride of calcium.

Mr Phillips' process.

The *London Pharmacopæia* directs the distillation of ether with potassa, for its purification from sulphurous acid; and Mr Richard Phillips, in his *Experimental Examination*, has given the following directions for procuring ether for pharmaceutical purposes, which answer extremely well.

"Mix with 16 ounces of sulphuric acid, an equal weight of rectified spirit, and distil about 10 fluid ounces, add 3 ounces of spirit to the residuum in the retort, and distil about 9 fluid ounces; or continue the operation until the contents of the retort begin to rise or the product becomes considerably sulphurous; mix the two products, and if the mixture consists of a light and heavy fluid, separate them: add potassa to the lighter, as long as it appears to be dissolved; separate the ether from the solution of potassa, and distil about nine tenths of it, to be preserved as *ether sulphuricus*, the specific gravity of which ought to be at most ,750."*

2064. Preparing ether upon a large scale, it is found that 14 parts of alcohol (specific gravity ,820) mixed with an equal weight of sulphuric acid (specific gravity 1,8,) and submitted to distillation, afford about 8 parts of impure ether (specific gravity, 770). To the residuum 7 parts of alcohol may be added, and about $7\frac{3}{4}$ parts more of impure ether drawn off. These products, when mixed, have a specific gravity of about ,782, and when rectified by distillation on carbonate of potassa, afford $10\frac{1}{4}$ parts of ether, of a specific gravity of ,735, and about $3\frac{1}{2}$ parts of ethereal spirit, which is employed instead of an equal quantity of alcohol in the next operation.

Washing of ether.

2065. When ether, obtained by the usual process, is washed with its bulk of water, its specific gravity is diminished, and the water employed for washing it affords, on distillation, a considerable portion of alcohol. By re-distilling this washed ether with a little potassa, which keeps down the water, or by treating it with chloride of calcium, it is obtained extremely light and pure.

Properties.

2066. Sulphuric ether is a transparent, colourless liquid, of a pleasant smell and a pungent taste; is highly exhilarating, and produces a degree of intoxication when its vapour is inhaled by the nostrils. Its specific gravity varies extremely with its purity. Lowitz is said to have procured it as light as ,730 and ,760.

Volatile.

It is extremely volatile, and when poured from one vessel into another, a considerable portion evaporates; during its evaporation from surfaces, it produces intense cold, as may be felt by pouring it upon the hand; and seen, by dropping it upon the bulb of a thermometer, which sinks to many degrees below

* In the preparation of ether on a large scale considerable risk is incurred by fire, recourse has therefore been had to steam as the source of the required heat. In the apparatus employed at Apothecaries' Hall (Lond.) the still is of cast-iron, lined with lead; the steam is conducted through the mixture of acids and alcohol by a contorted leaden pipe at the bottom of the still, and is supplied by a boiler calculated to resist the pressure of 100 lbs on the square inch: in this way the mixture is very rapidly raised to its boiling point, and a larger relative quantity of ether is obtained. The boiler is placed in a distant apartment. The condensing apparatus and refrigeratory are of the usual construction, but abundantly supplied with cold water.—*Brande's Pharmacy*, 456.

the freezing point. The specific gravity of the vapour of sulphuric ether, compared with atmospheric air, is according to Gay-Lussac, as 2,586 to 1,000.

At mean pressure, sulphuric ether, when of a specific gravity of ,730, boils at 98° , and under the exhausted receiver of an air-pump, at all temperatures above— 20° ; hence, were it not for atmospheric pressure, ether would only be known in the state of vapour. Boiling point.

In consequence of the cold produced during the vaporization of sulphuric ether, the phænomena of boiling and freezing may be exhibited in the same vessel.

For this purpose procure a very thin flask which fits loosely into a wine-glass, as shown in fig. 129. Pour a small quantity of ether into the flask, and of water into the glass, and place the whole under the receiver of an air-pump; during exhaustion, the ether will boil, and a crust of ice will gradually form upon the exterior of the flask. Exp. Pl. 7.

2067. Ether dissolves the resins, several of the fixed oils, and nearly all the volatile oils; it also dissolves a portion of sulphur, and of phosphorus; the latter solution is beautifully luminous when poured upon warm water, in a dark room. The fixed alkalies are not soluble in ether, but it combines with ammonia. Dissolves resins, &c.

By repeated agitation with water, ether is brought to a high degree of purity, and acquires the property of dissolving caoutchouc.* Washing of ether.

2068. Ether dissolves the oxides of gold and platinum, and these solutions have been employed for coating steel with those metals, with a view to ornament and as a defence from rust. If to a saturated solution of gold or platinum, in nitro-muriatic acid, there be added about three parts by measure of good sulphuric ether, it soon takes up the metals, leaving the acid nearly colourless below the ethereal solution, which is to be carefully decanted off; into this the polished steel is for an instant plunged, and immediately afterwards washed in water, or in a weak alkaline solution. Though the coating of platinum is the least beautiful, Mr Stodart, who has made many experiments upon this subject, considers it as the best protection from rust. Polished brass may be coated by the same process. These surfaces of gold and platinum, though very thin, are often a useful protection: with gold the experiment is particularly beautiful, and well illustrates the astonishing divisibility of the metal. The ethereal solution of gold is not permanent, but, after a time, deposits the metal in the form of a film, in which crystals of gold are often perceptible. Action on oxides of gold and platinum.

2069. Ether is sparingly soluble in water, and in alcohol it dissolves in all proportions. The *spiritus ætheris sulphurici* of the *Pharmacopœia*, is an alcoholic solution of ether.

2070. Ether is highly inflammable, and in consequence of its volatility it is often kindled by the mere approach of a burning Inflammable.

* The process is described in Henry's *Chemistry*, vol. ii. p. 359.

body ; a circumstance which renders it highly dangerous to decant, or open vessels of ether near a candle.*

The inflammability of ethereal vapour may be shown by passing a small quantity into a receiver, furnished with a brass stop-cock and pipe, and inverted over water at a temperature of 100°. The receiver becomes filled with the vapour, which may be propelled and inflamed ; it burns with a bright bluish white flame.

Explodes
with oxygen,

2071. When ether is admitted to any gaseous body it increases its bulk. Oxygen thus expanded, produces a highly inflammable mixture ; if the quantity of oxygen be large and of ether small, the mixture is highly explosive, and produces water and carbonic acid.

Into a strong two ounce phial, filled with oxygen gas, and wrapped round with a cloth, let fall a drop of ether. On applying the flame of a candle, a violent detonation will ensue.

and with
chlorine.

2072. The vapour of ether also explodes with chlorine, as is shown by the following experiment.

Exp.

Fill a bottle of the capacity of three or four pints, with chlorine gas, taking care to expel the water as completely as possible. Then throw into it about a drachm or a drachm and a half of good ether, covering its mouth immediately with a piece of light wood or paper. In a few seconds white vapour will be seen moving circularly in the bottle, and this will soon be followed by an explosion, accompanied with flame. At the same time a considerable quantity of carbon will be deposited, and the bottle will be found to contain carbonic acid gas.†

Analysis.

2073. Ether was analysed by M. Saussure, and from the data furnished by his analysis, corrected by Gay-Lussac,‡ ether is inferred to consist of 28 parts or two atoms of olefiant gas, and 9 parts or 1 atom of water. Alcohol is composed of 1 atom olefiant gas and 1 atom of water ; so that, if from two atoms of alcohol we withdraw one atom of water, the remaining elements are in exact proportion for constituting ether. This is the mode in which sulphuric acid is supposed to operate in generating ether. This view was first proposed by Fourcroy and Vauquelin.

Oil of wine.

2074. If ether be mixed with its bulk of sulphuric acid, and submitted to distillation, a portion of it is converted into a peculiar fluid which has been termed *oil of wine* ; it is the *oleum æthereum* of the *Pharmacopœia*. It has a sweetish taste, and a rich agreeable odour. It does not mix with water, but readily dissolves in ether and in alcohol. It is very inflammable, and deposits a large quantity of carbon during its combustion. Its composition has not been inquired into.

Sulpho-vinic
acid.

2075. The production of a peculiar acid in the preceding process was first noticed by M. Dabit, about the year 1800. This substance, to which the name *sulpho vinic acid* is applied, has since been examined by Sertuerner, Vogel and Gay-Lussac,

* In spirit warehouses or druggist's laboratories where ether is distilled, the *safety lamp* (fig. 118) may be advantageously used.

† Crickshank in *Nicholson's Jour.* 4to. v, 205. ‡ *Ann de Chim.* xcv.

and the two last regarded it as a compound of hypo-sulphuric acid and a peculiar vegetable matter. Mr Hennel, however, has lately given a different view of its nature. According to this chemist, sulphuric acid and the oil of wine are both composed of sulphuric acid and carburet of hydrogen. The oil of wine, which has no acid reaction when pure, consists of 2 atoms of sulphuric acid, 8 of carbon, and 8 of hydrogen. When heated, it parts with half of its carbon and hydrogen, and sulpho-vinic acid remains, consisting of 2 atoms of sulphuric acid, 4 of carbon, and 4 of hydrogen.*

2076. When ether is passed over red-hot platinum wire, or consumed in the lamp without flame, fig. 34, (199,) a peculiar acid substance is produced, which has been subjected to an interesting series of experiments, by Mr J. F. Daniell.† Pl. 2. He obtained it by placing the lamp, filled with ether, and properly trimmed with a coil of glowing platinum wire, under the head of an alembic, in which the vapour was condensed, and collected in a phial applied to its beak.

Mr Daniell called this substance *lampic acid* and its compounds *lampates*, but he has since found that it is merely acetic acid holding in solution some compound of carbon and hydrogen, which differs both from ether and alcohol.‡

b. NITRIC ETHER.

2077. When strong nitric acid and alcohol are mixed in equal proportions, a violent action presently ensues; there is a very copious evolution of an inflammable æriform body, which has been called *nitrous etherized gas*, and which appears to be a compound of nitrous ether, and nitric oxide. If we endeavour to condense the volatile products, we find that the receiver contains alcohol, water, nitrous ether, nitrous acid, and acetic acid; and that the greater portion of the true ether has made its escape with the gaseous products. Thenard has paid much attention to this subject, and has given the following process for obtaining nitric ether.§

Introduce into a sufficiently capacious retort equal weights of alcohol, (specific gravity 320) and of nitric acid of commerce (specific gravity 1.30) and connect it with five Woulfe's bottles, the first of which is empty, and the remaining four half filled with a saturated solution of salt in water. Apply a gentle heat to the retort, till the liquor begins to effervesce; then withdraw the fire, and the gaseous matter passing through the bottles, which should be kept cold by ice, deposits the ether upon the saline solution, from which it is to be decanted, shaken with chalk, and re-distilled at a very gentle heat.|| Preparation.

2078. Nitric ether, thus prepared, has the following properties: It has a very powerful ethereal odour; its colour is pale yellow; its taste very pungent; its specific gravity above that of alcohol, but less than that of water. It is more volatile than Properties.

* *Quart. Jour.* xxi. 331.

† *Ibid.* vi. 318

‡ *Ibid.* xii.

§ *Mém. d'Arcueil*, Tom. i. and *Traité de Chim.* iii.

|| See description of an apparatus for this process, by Dr Hare, in *Am. Jour.* vol. ii. p. 326.

sulphuric ether, and the heat of the hand is sufficient to produce its ebullition. It is soluble in 48 parts of water; and in all proportions in alcohol; this last solution is the *spiritus etheris nitrosi*, or *sweet spirit of nitre of the Pharmacopœia*. It is decomposed by keeping, and nitric and acetic acids are formed in it. According to Thenard, nitric ether consists of

| | |
|--------------------|-------|
| Oxygen | 48,52 |
| Carbon | 28,45 |
| Nitrogen | 14,49 |
| Hydrogen | 8,54 |

100,00

Composition. Dr Thomson* concludes, from analogy, that nitric ether consists of 4 proportionals of olefiant gas, = 28, and 1 of nitric acid, = 54; or, of

| | | |
|---|---------------------------|-------------------|
| 4 | proportionals of hydrogen | $1 \times 4 = 4$ |
| 4 | carbon | $6 \times 4 = 24$ |
| 1 | nitrogen | 14 |
| 5 | oxygen | $3 \times 5 = 15$ |
| | | — |
| | | 82 |

c. MURIATIC ETHER.

2079. Muriatic ether was thus obtained by Thenard:†

Preparation. Equal measures of strong liquid muriatic acid, and highly rectified alcohol, are put into a retort communicating with a receiver, from which a tube passes into a Woulfe's bottle containing warm water, and having a tube of safety: from this there issues a bent tube passing into a bottle surrounded by ice. On applying heat to the retort, a portion of alcohol and acid pass into the first receiver, and the ether in a gaseous state escapes through the warm water and the bent tube, and is condensed in the cold vessel.

Properties. 2080. At a temperature somewhat below 70° muriatic ether passes into the state of vapour, of which the specific gravity is about 2,220, that of air being 1,000; it is highly inflammable, its taste sweetish and ethereal, and it is soluble in its own bulk of water at 64°. Its specific gravity in a liquid state, at 40°, is ,870. It is remarkable that this ether does not affect vegetable blues, nor does it afford traces of chlorine to the usual tests; but, when burned, muriatic acid is immediately perceptible.

2081. This compound was supposed by Thenard to be analogous in composition to nitrous ether. It appears, however, from the experiments of M. M. Robiquet and Colin, that it consists of muriatic acid and the elements of olefiant gas, and is therefore quite free from oxygen.‡

d. HYDRIODIC ETHER.

2082. By distilling two measures of alcohol, with one of concentrated liquid hydriodic acid, Gay-Lussac obtained an ethereal liquid, of a specific gravity of 1,920 at 72°, and re-

* System, vol. ii. p. 341.

† Memoires d'Arcueil, Tom. i.

‡ Ann. de Chim. et de Phys. ii.

quiring a temperature of 148° for its ebullition. It appears to be similar in composition to muriatic ether.*

Acetous Fermentation.

2083. When any of the vinous liquors are exposed to the free access of atmospheric air at a temperature of 80° or 85° they undergo a second fermentation, terminating in the production of a sour liquid, called *vinegar*. During this process a portion of the oxygen of the air is converted into carbonic acid; hence, unlike vinous fermentation, the contact of the atmosphere is necessary, and the most obvious phenomenon is the removal of carbon from the beer or wine. Vinegar is usually obtained from malt liquor or cider, while wine is employed as its source in those countries where the grape is abundantly cultivated. Vinegar.

2084. The colour of vinegar varies according to the materials from which it has been obtained; that manufactured in England is generally artificially coloured with burnt sugar: its taste and smell are agreeably acid. Its specific gravity is liable to much variation; it seldom exceeds 1,0250. When exposed to the air it becomes mouldy and putrid, chiefly in consequence of the mucilage which it contains, and from which it may be in some measure purified by careful distillation. According to Mr R. Phillips,† when good malt vinegar of the specific gravity of 1,020 is distilled, the first eighth that passes over is of the specific gravity 0,997; the next six-eighths are of specific gravity 1,0023, and a fluid ounce decomposes 8,12 grains of precipitated carbonate of lime. The lightness of the first portion is owing to its containing alcohol, consequently, in the *Pharmacopœia* process it is ordered to be rejected. The term *distilled vinegar*, or *dilute acetic acid*, is properly applied to the second portion; it is erroneously called *acetic acid*, in the *London Pharmacopœia*. The matter which remains in the still is empyreumatic, and generally contains some other vegetable acids: when the vinegar has been adulterated, which is not unfrequently the case, we sometimes find in it muriatic and sulphuric acids. Properties.

2085. Distilled vinegar is colourless, and of a flat acid taste; it consists essentially of the real acid diluted with water. To obtain *acetic acid*, or, as it has been sometimes called, *radical vinegar*, distilled vinegar may be saturated with some metallic oxide, and the acetate thus obtained, subsequently decomposed. Acetic acid.

2086. Acetic acid is thus procured by distilling *acetate of copper*, or *crystallized verdigris*, in a glass retort heated gradually to redness: it requires re-distillation to free it from a little oxide of copper which passes over in the first instance. Acetic acid may also be obtained by distilling *acetate of soda* or *acq-*

* *Ann. de Chim.* xci.

† Remarks on the *London Pharmacopœia*.

tate of lead with half its weight of sulphuric acid : or from a mixture of equal parts of sulphate of copper and acetate of lead ; in these cases, the acid passes over at a moderate temperature.

Pyroligneous
acid.

2087. A considerable quantity of acetic acid is also now procured by the distillation of wood in the process of preparing charcoal for the manufacture of gunpowder. The liquor at first procured is usually termed *pyroligneous acid* ; it is empyreumatic and impure, and several processes have been contrived to free it from tar and other matters which it contains. It may be saturated with chalk and evaporated, by which an impure acetate (pyrolignate) of lime will be obtained, and which, mixed with sulphate of soda, furnishes, by double decomposition, sulphate of lime and acetate of soda ; the latter distilled with sulphuric acid affords a sufficiently pure acetic acid, which by dilution with water may be reduced to any required strength. The purification of this acid has been brought to great perfection by Dr Bollman.*

Pyroxylic
spirit.

2088. One of the products of the distillation of wood on a large scale, is a peculiar inflammable and volatile fluid resembling alcohol in some respects, but differing from it in others.† This fluid is colourless and transparent, its smell is strong, pungent, and ethereal, with a flavour of oil of peppermint. Its specific gravity, after being distilled from dry chloride of calcium is, 0,828. It boils at 150° F. When heated it burns with a fine blue flame. It is soluble in alcohol. Nitric acid and chlorine convert it into ether, endowed with peculiar properties. H.

To this fluid the name *pyroxylic spirit* has been given. It is used in lamps instead of alcohol.

Dr Thomson, from a mixture of pyroxylic spirit and aqua regia has obtained a new inflammable gas, which is composed of 1 atom of hydrogen, 1 of carbon and 1½ of chlorine, hence he calls it the *sesquichloride of carbo-hydrogen*.‡

Properties of
acetic acid.

2089. Acetic acid obtained by the processes described is transparent and colourless, its odour highly pungent and it blisters and excoriates when applied to the skin. Its specific gravity is 1,080. It is extremely volatile, and its vapour readily burns. It combines in all proportions with water, and when considerably diluted, resembles distilled vinegar. When highly concentrated, it crystallizes at the temperature of 38° F. but liquefies when its heat is a little above that point.

Apparatus for
preparing.

Pl. vii.

* The apparatus used in the preparation of this acid is represented by fig. 131 ; *a* is a section of the cylinder in which the wood, deprived of its bark, is placed ; *b* a different section, *c* the elevation of the furnace, *d* the outer stopper, *e* an inner shutter which is smeared round its edge with clay-lute, and secured to the mouth of the cylinder, *f* the pipe for conveying off the acid into the casks *g*, which are connected by the tubes *h*, *i* is the pipe for conveying the tar into the receiver *k*. The escape of the elastic fluids is provided for by bent tubes inserted in the casks, and terminating under the surface of water. The average quantity of impure acid obtained from each cwt. of wood is about four gallons and a half. The crude acid is rectified by a second distillation in a copper still.—See Parkes's *Essays*, i. 398.

† *Quart. Jour.* xiv. 436.

‡ *Edin. Jour.* xiii. 182.

The most probable constitution of acetic acid, derived from the analysis of its salts, is the following :

| | Atoms. | | | | Composition. |
|----------|--------|----|-----|--|--------------|
| Carbon | 4 | 24 | 48 | | |
| Oxygen | 3 | 24 | 48 | | |
| Hydrogen | 2 | 2 | 4 | | |
| | | 50 | 100 | | |

Its equivalent, according to this view of its composition, is 50. H. 2. 372.

2090. The acetates are all soluble in water, and mostly very soluble : many of them are deliquescent, and difficultly crystallizable; they are decomposed by sulphuric acid, and when submitted to destructive distillation, furnish a modified vinegar, which has been termed *pyroacetic acid* or *spirit* : these decompositions have been fully investigated, and the properties of the pyroacetic spirit inquired into, by Mr Chenevix.*

The following are among the most important of the acetates:

2091. *Acetate of Ammonia* is a very deliquescent, soluble salt, and extremely difficultly crystallizable. In solution, obtained by saturating distilled vinegar with carbonate of ammonia, it constitutes the *ammonix acetis liquidus* of the *U. S. P.* which has long been used in medicine as a diaphoretic, under the name of *spirit of Mindererus*. — of ammonia,

2092 *Acetate of Potassa* is usually formed by saturating distilled vinegar with carbonate of potassa, and evaporating to dryness. If this salt be carefully fused, it concretes into a lamellar deliquescent mass on cooling. It is the *terra foliata tartari*, and *febrifuge salt of Sylvius* of old pharmacy. It dissolves in its own weight of water at 60°. and the solution has an acrid saline taste. It consists of one proportional of each of its components. — of potassa,

2093. *Acetate of Soda* forms prismatic crystals, not deliquescent, of an acrid bitterish taste, and soluble in rather less than three parts of water at 60°. It is the *terra foliata crystallisata* of old writers. It consists of 32, soda + 50 acetic acid. — of soda,

2094. *Acetate of Lime*, is a difficultly crystallizable salt, readily soluble in water, and of a bitter saline taste; consisting of 28 lime + 50 acid. It is sometimes obtained by saturating the vinegar formed during the distillation of wood, and employed in the preparation of *acetate of alumina*, which is used by the calico-printers as a mordant. — of lime,

2095. *Acetate of Baryta* furnishes crystals of a sour and bitterish taste:† in cold weather the concentrated solution congeals into a silky congeries of crystals. It requires rather more than its own weight of water at 60° for solution, and consists of 50. acid + 78, baryta. — of baryta,

2096. *Acetate of Iron*.—The acetic acid combines with both oxides of iron. The *protacetate* is formed by digesting — of iron,

* *Annales de Chimie*, xlix. † For their form, see *Ann. Philos.* N. S. vii 365.

sulphuret of iron in acetic acid; it yields green prismatic crystals, of a styptic taste, and readily soluble in water; the solution becomes brown by exposure to air, and passes into *peracetate*, which is uncrystallizable, and obtained by digesting iron in acetic acid. This compound is extensively used by calico-printers, who prepare it either by digesting iron in pyroligneous acid, or by mixing solution of acetate of lead with sulphate of iron, and exposing the filtered solution to air.

Acetate of
zinc,

2097. *Acetate of Zinc*, is formed either by dissolving oxide of zinc in acetic acid, or by mixing a solution of sulphate of zinc with one of acetate of lead. It crystallizes in thin shining plates of a bitter and metallic taste, very soluble, but not deliquescent. This salt is sometimes used in pharmacy, chiefly as an external application.*

— of tin,

2098. *Acetate of Tin*.—This mineral is slowly acted on by acetic acid, but a *protacetate* and *peracetate of tin* may be made by mixing acetate of lead with saturated solutions of the protomuriate and permuriate of tin. These solutions have been recommended as mordants for the use of dyers. The protacetate is crystallizable. Vinegar kept in tin vessels dissolves a very minute portion of the metal; and in pewter vessels it likewise dissolves a small portion of the lead, where in contact both with the vinegar and air; hence distilled vinegar, which has been condensed in a pewter worm, affords generally traces of both metals.†

— of copper,

2099. *Acetate of Copper*.—By exposing copper to the fumes of vinegar, it becomes gradually incrustated with a green powder called *verdigris*,‡ which is separable by the action of water into an insoluble *subacetate of copper*, and a soluble *acetate*.

Acetate of copper may be obtained by digesting verdigris, or oxide of copper, in acetic acid; by evaporating this solution, it is obtained in prismatic crystals of a fine green tint. It dissolves sparingly in water and alcohol, and communicates a beautiful blue-green colour to the flame of the latter; by distillation it affords a very pure acetic acid.

— of lead.

2100. *Acetate of Lead*, is the *Sugar of Lead*, and *Salt of Saturn* of the old chemists: it may be regarded as the most important of the acetates; it is used in pharmacy, and by dyers and calico-printers for the preparation of acetate of alumina and of iron, which are formed by mixing its solution with that of the sulphates of those metals, an insoluble sulphate of lead being at the same time produced. Acetate of lead is formed by digesting the carbonate in distilled vinegar, or in the acetic acid obtained by the destructive distillation of wood; it usually

* According to Messrs Aikin, the specific gravity of a saturated solution of acetate of zinc, made by digesting the salt in distilled vinegar, is 1055. Of this solution 900 grains contain 53 of dry, or 82.6 of crystallized acetate. One ounce by measure of the solution weighs 506 grains, and contains 29.8 grains of dry, or 46.5 grains of crystallized salt.

† Vauquelin, *Annales de Chimie*, xxxii.

‡ *Diacetate*, T —For a description and analysis of the acetates of copper see Thomson's *First Principles*, ii. 383.

occurs in masses composed of acicular crystals; but by careful crystallization it may be obtained in quadrangular prisms. Its taste is sweet and astringent, and it is soluble in about four parts of water at 60°.

The crystals effloresce slowly by exposure to the air, and are composed, according to Berzelius and Thomson, of 50 parts or one atom of the acid, 112 parts or one atom of the protoxide of lead, and 27 parts or three atoms of water.

2101. The acetate of lead is partially decomposed, with formation of the carbonate of lead, by water which contains carbonic acid, or by exposure to the air; but a slight addition of acetic acid renders the solution quite clear.

2102. The *sub-acetate* of lead, commonly called *extractum saturni*, is prepared by boiling one part of the neutral acetate, and two parts of litharge, deprived of carbonic acid by heat, with 25 parts of water. This salt is less sweet and less soluble in water than the neutral acetate, has an alkaline reaction and crystallizes in white plates by evaporation. It is decomposed by a current of carbonic acid, with production of pure carbonate of lead; and forms a turbid solution. It appears from the analysis of Berzelius to consist of 1 atom of acid and 3 atoms of the oxide of lead.

Sub-acetate of lead.

A *di-acetate* may be formed by boiling with water a mixture of litharge and acetate of lead in atomic proportions.*

2103. *Acetate of Mercury*.—*Protacetate of Mercury* is most readily formed by mixing a solution of protonitrate of mercury with acetate of potassa. For this purpose dissolve three ounces of mercury in about four ounces and a half of cold nitric acid, and mix this solution with three ounces of acetate of potassa previously dissolved in eight pints of boiling water, and set the whole aside to crystallize, which takes place as the liquor cools, and the acetate of mercury then separates in the form of micaceous crystalline plates, which are to be washed in cold water, and dried on blotting paper.† In preparing this salt, the quantity of water for dissolving the acetate need not be so large as above directed, one pint being sufficient, but it is necessary to pour the mercurial solution into the acetate. This salt has an acrid taste, and is very difficultly soluble in water, requiring according to Braconnot,‡ 600 parts of water. It is insoluble in alcohol. It was once used in medicine.§

Acetate of mercury.

* Thomson.

Dr Thomson has described several acetates of lead, for an account of which see *First Principles*, vol. ii.

† *Edinburgh Pharmacopœia*.

‡ *Annales de Chimie*, lxxxvi. 92.

§ *Peracetate of Mercury* is formed by digesting the peroxide in acetic acid; it does not crystallize and affords on evaporation a deliquescent yellow mass, which is decomposed by water into a *super-acetate*, which remains dissolved, and an insoluble *subperacetate*. (a) *Acetate of Silver* is obtained by boiling the acid on oxide of silver, or by mixing solutions of acetate of potassa and nitrate of silver; it forms acicular crystals of an acrid metallic taste.

a Proust, *Journal de Phys.* lvi.

Acetate of
alumina.

2104. *Acetate of Alumina*.—This salt is extensively employed by calico-printers as a mordant or basis for fixing colours; they produce it by mixing solutions of alum and acetate of lead: about three pounds of alum are dissolved in eight gallons of water and a pound and a half of sugar of lead stirred into it; a copious formation of sulphate of lead ensues which is allowed to subside, and the clean liquor holding acetate of alumina and a portion of undecomposed alum in solution, is then drawn off, a portion of pearlash and chalk being added to it previous to use, in order to saturate any excess of acid.

Acetate of alumina, formed by digesting recently precipitated alumina in acetic acid, may be procured in deliquescent acicular crystals of an astringent taste, and containing, according to Richter, 73,81 acid + 26,19 alumina: hence it is probably a *binacetate*.

Acetic ether.

2105. When acetic acid and alcohol are repeatedly distilled together, a portion of *acetic ether* is formed, which has a peculiar and agreeable taste and smell, and a specific gravity of about ,860 at 60°. It boils at about 160°, is highly inflammable, and emits acetic acid among its products of combustion.*

Acetic ether is much more soluble in water than sulphuric ether: according to M. Thenard, water at 60° dissolves about a 7,5 parts of its weight, and the solution is permanent. Caustic potassa decomposes it, and forms acetate of potassa.

Oxalic, citric, tartaric, and benzoic acids have been employed in the formation of ethers; the presence of a mineral acid is indispensable to their formation.†

CHAPTER VII.

OF ANIMAL SUBSTANCES.

2106. THE different sections of this chapter will contain an account of the ultimate and proximate principles of the substances belonging to the animal creation, of the methods of analysis by which these principles are obtained, and of such of the animal functions as are concerned in their production, where these are susceptible of chemical elucidation.

* This ether is directed in some of the foreign Pharmacopœiæ for medical use, and the following is perhaps the best process for its production. Introduce into a tubulated retort 3 parts of acetate of potassa, 3 of alcohol, and 2 of sulphuric acid, and distil to dryness. To the product add one-fifth its weight of sulphuric acid, and draw off by a gentle heat a quantity of ether equal to that of the alcohol originally employed.

† Ure's Dictionary, Art Ether.

SECTION I. *Of the ultimate Principles of Animal Matter, and of the products of its destructive Distillation.*

2107. The proximate principles of the animal creation consist, like those of vegetables, of a few elementary substances, which by combination in various proportions, give rise to their numerous varieties. Carbon, hydrogen, oxygen, and nitrogen, are the principal ultimate elements of animal matter; and phosphorus and sulphur are also often contained in it. The presence of nitrogen constitutes the most striking peculiarity of animal, compared with vegetable bodies; but as some vegetables contain nitrogen so there are also certain animal principles, into the composition of which it does not enter.

Proximate principles.

Nitrogen.

2108. The presence of nitrogen stamps a peculiarity upon the products obtained by the destructive distillation of animal matter, and which are characterized by the presence of ammonia, formed by the union of the hydrogen with the nitrogen. It is sometimes so abundantly generated as to be the leading product; thus, when horn, hoofs, or bones, are distilled *per se*, a quantity of solid carbonate of ammonia, and of the same substance combined with empyreumatic oil, and dissolved in water, are obtained; hence the pharmaceutical preparations called *spirit* and *salt of hartshorn*, and Dippel's *animal oil*. Occasionally the acetic, benzoic, and some other acids are formed by the operation of heat on animal bodies, and these are found united to the ammonia; cyanogen and hydrocyanic acid also frequently occur.

Ammonia.

If the gas evolved during the decomposition of animal bodies be examined, it is generally inflammable, and consists of carburetted hydrogen, often with a little sulphuretted and phosphuretted hydrogen; carbonic oxide, carbonic acid, and nitrogen, are also sometimes detected in it.

Carburetted hydrogen.

The coal remaining in the retort is commonly very difficult of incineration, a circumstance depending upon the common salt and phosphate of lime, which it usually contains, forming a glaze upon its surface which defends the carbon from the action of the air. Animal charcoal is also found to be more effectual in destroying colour and smell, than that obtained from vegetables.

2109. By the term *putrefaction* we mean the changes which dead animal matter undergoes, and by which it is slowly resolved into new products. These changes require a due temperature, and the presence of moisture; for below the freezing point of water, or when perfectly dry, it undergoes no alteration.

Putrefaction.

During putrefaction the parts become soft and flabby, they change in colour, exhale a nauseous and disgusting odour, diminish considerably in weight, and afford several new pro-

ducts, some of which escape in a gaseous form, others run off in a liquid state, and others are contained in the fatty, or earthy residuum.

Antiseptics.

The presence of air, though not necessary to putrefaction, materially accelerates it, and those gases which contain no oxygen, are very efficient in checking or altogether preventing the process. Carbonic acid also remarkably retards putrefaction; and if boiled meat be carefully confined in vessels containing that gas, it remains for a very long time unchanged, as seen in M. Appert's method of preserving meat.

There are several substances which, by forming new combinations with animal matter, retard or prevent putrefaction, such as chlorine and many of the saline and metallic compounds; sugar, alcohol, volatile oils, acetic acid, and many other vegetable substances also stand in the list of anti-putrefactives, though their mode of operating is by no means understood.

Effect of the effluvia.

2110 The effluvia which arise from putrescent substances, and more especially those generated in certain putrid disorders, have a tendency to create peculiar diseases, or to give the living body a tendency to produce poisons analogous to themselves.

Fumigation.

An atmosphere thus tainted by infectious matter, may be rendered harmless by fumigation with the volatile acids, more especially the nitrous and the muriatic; chlorine is also very effectual: the vapour of vinegar, though sometimes useful in covering a bad smell, is not to be relied on. It appears evident that the acid and chlorine act chemically upon the pernicious matter, and resolve it into innocuous principles.

Adipocere.

2111. When muscular flesh is immersed in a stream of running water, it is partially converted into a substance having many of the properties of fat combined with a portion of ammonia. The same changes have been observed where large masses of putrefying animal matter have been heaped together, or where water has had occasional access to it. Nitrate of ammonia is also sometimes formed under the same circumstances.

2112. Instead of considering the proximate principles of animals under separate sections, as has been done in regard to vegetable bodies, they may be made known under the heads of those substances in which they occur, the principal of which are the following:

- | | |
|--------------------------------------|----------------------------------|
| 1. Blood. Albumen. Colouring Matter. | 6. Skin. Membrane. |
| 2. Milk. Sugar of Milk. | 7. Muscle. Ligament. Horn. Hair. |
| 3. Bile. Resin of Bile. | 8. Fat. Spermaceti, &c. |
| 4. Lymph. Mucus. Synovia, Pus, &c. | 9. Cerebral substance. |
| 5. Urine. Urea. Urinary Calculi. | 10. Shell and Bone. |

SECTION II. *Of the Blood.*

2113. In the higher orders of animals the blood is of a red colour, florid in the arteries, and dingy in the veins. The specific gravity of human blood is liable to some variation. Mr Brande has found it as low as 1,050 and as high as 1,070, but was unable to refer to any circumstances which might be considered as the cause of this difference.

When blood is drawn from its vessels in the living animal, it soon concretes into a jelly-like mass, which afterwards gradually separates into a fluid *serum*, of a pale straw colour, and a coagulated *crassamentum* or *cruor*, which is red. The cause of this coagulation is quite unknown.

Serum and crassamentum.

2114 The specific gravity of the serum of the blood, is upon an average 1,030. It reddens the yellow of turmeric, and changes the blue of violets to green, a property derived from a portion of soda. At a temperature of 160°, it becomes a firm yellowish white coagulum, resembling in appearance and properties the coagulated white of an egg, and, as the principle to which this property is owing is the same in both substances, it has been called *albumen*. Alcohol, and many of the acids, also occasion the coagulation of the serum of blood.

Properties of serum.

100 parts of human serum contain between eight and nine parts of albumen, rather less than one part of carbonate of soda, and about the same quantity of common salt, the remaining 90 parts being water. These at least are the proportions which Mr Brande's experiments lead him to believe correct; but the analysis is involved in so much difficulty that he considers the results only as approximating to the truth; indeed it is probable that the composition of the serum is liable to much variation.*

2115. *Albumen*, which constitutes a leading ingredient in the serum, and which we shall presently find also in the *cruor*, is a very important animal principle, and is found in the greater number of animal fluids.

Albumen.

Liquid Albumen is soluble in water, and always contains a notable portion of soda, indicated by its action on vegetable colours. It is coagulated by heat, acids, and alcohol, unless it

* Dr Marcet and Berzelius have each given an analysis of the serum of human blood; the following are their results.

| Marcet. | | | | Berzelius. | | | |
|------------------------------|---|---|---------|---------------------------------------|---|---|--------|
| Water | - | - | 900, | Water | - | - | 905,0 |
| Albumen | - | - | 86,8 | Albumen | - | - | 80,0 |
| Muriates of potassa and soda | - | - | 6,5 | Muriates of potassa and soda | - | - | 6,0 |
| Muco extractive matter | - | - | 4,0 | Lactate of soda, with animal matter | - | - | 4,0 |
| Carbonate of soda | - | - | 1,65 | Soda and phosphate of soda with ditto | - | - | 4,1 |
| Sulphate of potassa | - | - | 0,35 | Loss | - | - | 0,9 |
| Earthy phosphates | - | - | 0,60 | | | | |
| | | | 1000,00 | | | | 1000,0 |

Medico Chirurgial Transactions, vol. ii. Annals of Philosophy, vol. ii.

be considerably diluted with water, in which case a portion separates in the form of white flakes after some hours' standing. Solution of corrosive sublimate, added to albumen, very much diluted, produces a cloudiness, and hence it is a useful test of albumen.* It is also instantly coagulated by Voltaic electricity; and if two platinum wires connected with a small battery be immersed into diluted albumen, a very rapid coagulation will take place at the negative pole, and scarcely any effect at the positive pole. This circumstance induced Mr Brande to attribute the coagulation to the removal of the alkali, by alcohol, and by acids; but how heat operates is not very obvious, unless we be allowed to consider it as effecting a kind of decomposition of the liquid albumen. We might thus consider liquid albumen as a compound of albumen and soda dissolved in water: the effect of heat would then be to transfer the soda to the water, and thus occasion a coagulation; and a solution of soda is always found oozing from coagulated serum, and has sometimes been called *serosity*; in time it re-acts upon the coagulum, and dissolves a portion of it.

2116. When albumen is dried in a moderate heat, it shrinks and becomes brown and semi-transparent, resembling horn in appearance and properties. In this state it scarcely dissolves in boiling water, though it gradually softens; it is not prone to decomposition; it dissolves in the alkalies, a portion of ammonia being evolved and a saponaceous compound formed. Dilute nitric acid converts it into a substance having the properties of gelatine.†

By destructive distillation albumen furnishes a variety of products characterized by the presence of a large proportion of ammonia. According to Gay-Lussac and Thenard,‡ its ultimate constituents are

| | |
|--------------------|--------|
| Carbon | 52,883 |
| Oxygen | 23,872 |
| Hydrogen | 7,540 |
| Nitrogen | 15,705 |

100,000

2117. When the coagulum of the blood is carefully washed under a small stream of water, the colouring matter is gradually dissolved, and washed out of it, and a white fibrous substance remains, which has been termed *fibrina* or *coagulable lymph*, but of which the chemical properties are those of albumen.

It sometimes happens, when the blood is long in coagulating, as in certain inflammatory diseases, that a portion of this albumen is left without the colouring matter, forming what has been called the *buffy coat of blood*; in this case it is so tough as to admit of being removed from the coloured portion, and when dried, shrinks up, and appears exactly like horn.

* Bostock, Nicholson's *Journal*, xiv.

† Hatchett, *Phil. Trans.* 1800.

‡ *Recherches Physico-chymiques*.

Coagulated
by Voltaic
electricity.

Effect of
heat.

Products of
its distilla-
tion.

Fibrin.

Buffy coat.

Although the cause of the spontaneous coagulation of blood be unknown, the process consists in a portion of the albumen separating in a solid form along with the colouring matter, while another portion remains dissolved in the serum; this effect is somewhat analogous to the crystallization of a saline solution, in which one portion of the salt separates, while another remains dissolved.

2118. Much uncertainty prevails among chemists relative to the cause of the colour of the red globules of blood. It has been ascribed to the presence of peroxide of iron, an opinion adopted by Fourcroy and Vauquelin. The subject was investigated in 1812 by Berzelius: on comparing together the composition of the three principal ingredients of the blood he found that the ashes of the colouring matter always yielded oxide of iron in the proportion of $\frac{1}{200}$ th of the original mass, while the oxide was entirely wanting in the fibrin and albumen. Hence it was inferred that iron is concerned in the production of the red colour.

Cause of colour.

Berzelius' experiments.

Mr Brande* obtained results quite contrary to those of Berzelius. He detected iron in the ashes of the serum and fibrin, as well as in those of the red globules, and in each it was present in such minute quantity, that no effect as a colouring agent could be expected from it. Mr Brande supposed that the tint of the red globules is produced by a peculiar animal colouring principle, capable, like other substances of a similar nature, of combining with metallic oxides.

Brande's experiments.

The conclusions of Mr Brande received additional support from the researches of Vauquelin,† but the question has been finally decided by Dr Engelhart.‡ He demonstrated that the fibrin and albumen of the blood, when carefully separated from colouring particles, do not contain a trace of iron; on the contrary, he procured iron from the red globules by incineration. He has likewise proved the existence of iron in the colouring matter of blood by the liquid tests; for, on transmitting a current of chlorine gas through a solution of red globules, the colour entirely disappeared, white flocks were thrown down, and a transparent solution remained, in which the peroxide of iron was discovered by the usual reagents. These facts have been since confirmed by M. Rose.

Engelhart's experiments.

2119. Dr Engelhart has procured the colouring matter of the blood in a pure state by a method founded on the fact, that serum, when much diluted, does not coagulate by heat, while the red particles are coagulated, and fall down in the form of brown flocks. Serum diluted with ten parts of water does not coagulate at 167° F. but the colouring matter, dissolved in fifty parts of water, begins to coagulate at 149°. T. 636.

2120. Besides the principles now enumerated, and which may be considered as essential to the blood, it often contains

Blood contains carbonic acid.

* Phil. Trans. 1812. † Ann. de Chim. et de Phys. i. ‡ Edin. Med. and Surg. Jour. Jan. 7, 1827.

carbonic acid, which escapes when the blood is gently heated, or placed under the exhausted receiver of the air-pump.

Experiments on the blood, in different diseases, have thrown no light whatever on their nature, nor have any material differences been found in the blood of the same animal at different periods, or in that of different animals of the same class.

SECTION III. Milk.

2121. The chemical properties of this secretion differ somewhat in different animals. The milk of the cow has been most attentively examined, and it has the following properties :

Properties.

It is nearly opaque; white, or slightly yellow; of an agreeable sweetish taste, and a peculiar smell. Its specific gravity varies from 1018 to 1020. It boils at a temperature a little above that of water, and freezes at 32°. When allowed to remain a few hours at rest, a thick unctuous liquid collects upon its surface called *cream*; the colour of the remaining milk becomes bluish white, and when heated to about 100° with a little *rennet* it readily separates into a *coagulum* or *curd*, and a *serum* or *whey*. In this way the three principal constituents of milk are separable from each other.

Butter.

2122. By the process of churning, cream is separable into *butter*, and *butter-milk*, the latter being the whey united to a portion of curd.*

Butter may be considered as an animal oil, containing a small portion of curd and whey. It liquefies at about 98°, and by this process the impurities are separated, and it remains a longer time without becoming rancid.

Curd.

2123. The *curd* of milk has the leading properties of coagulated albumen, and, like that principle, is coagulable by alcohol and acids, and is also similarly affected by Voltaic electricity; heat slowly produces the same effect, and by boiling milk, the albumen separates in successive films.

Cheese.

2124. Curd, in combination with various proportions of butter, constitutes the varieties of *cheese*; that containing the largest quantity of oil becomes semi-fluid when heated; bad cheese which consists of little else than curd or albumen, shrinks and dries when heated, curling up like a piece of horn.

Aposepedine.

2125. The products of the fermentation of cheese have been examined by M. Braconnot, who has shown that the substance called by Proust *caseous oxide* has no claim to such a title, and proposes to call it *Aposepedine*, from *απο* and *σηπεδον*, (result of putrefaction). To obtain this substance the curd of skim-milk

* According to Berzelius, 100 parts of cream, of the specific gravity of 1024, consist of

| | | |
|--------|-----------|-------|
| Butter | - - - - - | 4,5 |
| Curd | - - - - - | 3,5 |
| Whey | - - - - - | 92,0 |
| | | 100,0 |

spontaneously coagulated is to be mixed with water and exposed in an open vessel until the putrefaction has fully attained its height. By filtration a liquid is obtained which, on being concentrated by evaporation; yields a product of a very fetid odour, owing apparently to the presence of an oily substance. Towards the close of the evaporation vapours of acetic acid pass over, and a liquid of the consistence of sirup remains, which on cooling concretes into a granulated reddish mass like honey, and of a saline bitter taste. Treated by alcohol it is separated into a soluble and insoluble portion. The latter is the *Aposepedine* of M. Braconnot, the former is the *caseate of ammonia* of Proust.

2126. *Aposepedine* when pure is in the form of a white powder, inodorous and of a slight bitter taste. It is heavier than water, and soluble in 14 parts of water at 123° F. By spontaneous evaporation this substance crystallizes either in the form of elegant dendritic ramifications, or in rings composed of delicate acicular crystals of a silky lustre. It takes fire when strongly heated, and burns with flame having no residue. The presence of sulphur is demonstrated by the formation of sulphuretted hydrogen, and by rubbing a piece of silver with it while heated, when the sulphuret of silver is formed. Properties.

From these and other facts* it appears to possess the characters of an animal substance. M. Braconnot considers it to be formed during the putrefaction of all animal matters: it is also generated in some diseases.

2127. *Caseic Acid*.—The substance called *caseate of ammonia* by Proust and separated by the action of alcohol from impure caseous oxide or *aposepedine*, appears to be a very complex substance. The alcoholic solution, on standing for about a month, deposited a little animal matter which Proust supposed to be gum. It yielded likewise flattened hexaedral crystals of phosphate of soda and ammonia, derived, M. Braconnot conceives, from the serum contained in the curd. The alcoholic solution, after depositing the double phosphate, was found to contain the following substances: 1. Free acetic acid; 2. *Aposepedine*; 3. Animal matter soluble in water and insoluble in rectified alcohol;† 4. Animal matter soluble both in water and alcohol; 5. Yellow oil, fluid and pungent; 6. Brown resin; 7. Acetate of potassa; 8. Muriate of potassa; and traces of the acetate of ammonia. The caseic acid of Proust has therefore no existence; and the acidity of the supposed compound is owing to acetic acid, while its pungency is chiefly occasioned by the yellow oil.‡ Caseic acid.

2128. *Whey* is a transparent fluid of a pale yellow colour and a sweetish flavour; by evaporation it affords a minute quantity of saline matter, and a considerable portion of sugar of milk. Whey.

* See an abstract of M. Braconnot's memoir in *Edin. Philos. Jour.* xvi. 367.

† Supposed to be osmazome.

‡ *Ann. de Chim. et de Phys.* xxxv. 159.

Koumiss.

2129. In some cases whey may be made to undergo vinous fermentation; and the Tartars, it is said, prepare a kind of wine from the whey of mare's milk, which they call *Koumiss*.*

Sugar of milk.

2130. *Sugar of Milk* may be obtained in white rhomboidal crystals, of a sweet taste, and soluble in seven parts of water at 60°, but insoluble in alcohol. When exposed to heat, it affords nearly the same products as common sugar. It consists, according to Berzelius, when deprived of water, of

| | |
|--------------------|---------|
| Carbon | 45,267 |
| Oxygen | 48,348 |
| Hydrogen | 6,385 |
| | <hr/> |
| | 100,000 |

2131. It is not susceptible of undergoing the vinous fermentation; and when digested with nitric acid it yields the *saccho-lactic acid*, a property first noticed by Scheele, and which distinguishes the saccharine principle of milk from every other species of sugar. Like starch, it is convertible into real sugar by being boiled in water acidulated with sulphuric acid. The sugar of milk contains no nitrogen, and according to the analysis of Gay-Lussac and Thenard, is very analogous to common sugar in the proportion of its elements. T.

Sactates.

2132. The *saccholates*, or *sactactates*, have scarcely been examined. With ammonia, potassa, and soda, this acid forms crystallizable compounds, more soluble than the acid. The sactates of lime, baryta, and strontia, are insoluble, as are those of silver, mercury, and lead.

Lactic acid.

2133. When milk or whey are exposed to a temperature between 60° and 80°, they undergo a spontaneous change, attended by the production of an acid, which was originally examined by Scheele, and has been termed *lactic acid*. Fourcroy and Vauquelin have shown reason to suspect its peculiar nature, and were led to regard it as identical with the acetic acid. Berzelius has more recently revived the opinion of Scheele, but Prof. Brande is induced from his own experiments to believe, that if it be not the acetic acid originally, it becomes so by combination with a base, and subsequent separation by sulphuric acid.

SECTION IV. *Bile*.

Properties.

2134. This secretion is formed in the liver, from venous blood. It is an unctuous liquid, of a yellowish green colour, and its specific gravity is between 1020 and 1030. Its taste is intensely bitter, and it readily putrefies, exhaling a most nauseous odour.

2135. According to Thenard the bile of the ox consists of three distinct animal principles, a yellow colouring matter, a

* *Edinburgh Phil. Trans.* vol. ii.

species of resin, and a peculiar substance, to which, from its sweetish bitter taste, he has applied the name of *picromel*. According to his analysis 800 parts of bile consist of water 700 parts, resin 15, picromel 69, yellow matter about 4, soda 4, phosphate of soda 2, muriates of soda and potassa 3,5, sulphate of soda 0,8, phosphate of lime and perhaps magnesia 1,2, and a trace of oxide of iron. He supposed the resin to be combined with the picromel and soda, and ascribes its solubility in water to this cause.

Berzelius denies that this fluid contains any resinous principle, and regards the yellow matter, resin, and picromel of Thenard, as one and the same substance, to which he applies the name of *Biliary matter*.*

2136. *Biliary Calculi* are of two kinds; those which most commonly occur, are soft, fusible, and of a crystalline texture, and inflammable. They have generally been considered as closely resembling spermaceti; they are soluble in boiling alcohol, in ether, and difficultly in oil of turpentine. Chevreul, having remarked some peculiarities in this substance, is induced to regard it as a peculiar animal principle, and distinguishes it by the name of *cholesterine*.

Biliary calculi.

Cholesterine.

2137. Cholesterine is fusible at 280° , and on cooling concretes into a crystalline mass; rapidly heated to about 400° , it evaporates in dense smoke; it is insoluble in water, and nearly so in cold alcohol; boiling alcohol dissolves about $\frac{1}{20}$ th its weight. It is soluble in nitric acid; but not convertible into soap by the alkalies.

2138. The other kind of biliary calculus resembles inspissated bile in appearance, but differs from it in being insoluble in alcohol and water. It is often mixed with variable proportions of the former, constituting biliary calculi of intermediate characters.

2139. The gall-stone of the ox is nearly insoluble in water and alcohol, and appears to consist chiefly of the yellow matter of bile; painters sometimes use it as a yellow pigment.

2140. *Erythrogen*.—This substance was discovered in 1821 by M. Bizio of Venice, in a peculiar fluid, quite different from bile, which was found in the gall-bladder of a person who had died of jaundice. It is of a green colour, transparent, tasteless, and of the odour of putrid fish. It is unctuous to the touch, may be scratched or cut with facility, and has a specific gravity of 1,57. It fuses at 110° F. and at 122° rises in vapour. It is insoluble in water and ether, but readily dissolved by hot alcohol, and the solution yields crystals. When put into nitric acid of the temperature of about 120° or 140° F. its green tint disappears, effervescence, owing to the escape of oxygen gas, ensues, and the solution acquires a deep purple colour. A similar phenomenon takes place, with disengagement of hydro-

Erythrogen.

* *Med. Chir. Trans.* iii.

gen gas, when erythrogen is digested in a solution of ammonia, and when volatilized in the open air, it yields a purple coloured vapour. M. Bizio is of opinion that the erythrogen, unites with nitrogen, and that the product is identical with the colouring matter of the blood. The production of the red compound is characteristic of erythrogen, and suggested the name by which this substance is designated, *Erythros ruber*.* T.

SECTION V. Lymph, Mucus, Pus, &c.

Lymph.

2141. The liquid which lubricates the different cavities of the body, which is contained in the lymphatics, and which occasionally forms the chief contents of the thoracic duct, has been termed *lymph*. It is colourless, transparent, miscible in all proportions with water, does not affect vegetable blues, is not coagulated by acids or alcohol, but only rendered slightly turbid by the latter. It has the characters of a very weak solution of albumen.

The fluid which collects in cases of dropsy and in vesications is of a similar nature, but the proportion of albumen is liable to variation, and hence it is differently influenced by tests; when very rapidly thrown out from inflamed surfaces, it sometimes furnishes a coagulum, apparently as abundant as that of the serum of the blood.

Mucus.

2142. The term *mucus* has sometimes been applied to these fluids when they have undergone a certain degree of inspissation; at other times, it has been used to designate a very alkaline albuminous fluid. Dr Bostock has pointed out some circumstances in which mucus differs from liquid albumen, and has proposed subacetate of lead as a test for its presence.† But that salt is so easily decomposed by many vegetable and animal substances, as to render it of doubtful efficacy for this purpose.

Saliva.

2143. *Saliva* consists, according to Dr Bostock,‡ of

| | |
|--------------------|----|
| Water | 80 |
| Coagulated albumen | 8 |
| Mucus | 11 |
| Saline substances | 1 |

100

Mr Brande found that it was copiously coagulable by the action of Voltaic electricity, and was hence induced to consider the mucus as a peculiar albuminous combination, not coagulable by the usual means.§

Pancreatic juice.

2144. The *Pancreatic juice* has not been minutely examined, but from the experiments of Dr Fordyce, it would appear to differ little from saliva.

* *Quart. Jour.* xvi. † *Nicholson's Journal*, vol. ix. ‡ *Nicholson's Journal*, vol. xiv.
§ *Phil. Trans.* 1809.

2145. *Tears* contain a small portion of albumen combined with soda, muriate of soda, and water. There are also small portions of other salts. Tears.

2146. *The humours of the eye.*—The *aqueous humour* is composed of water holding a minute quantity of albumen and saline matter in solution; the *crystalline lens* also contains more than half its weight of water, the remainder being an albuminous substance with traces of muriates. Humours of the eye.

2147. *Synovia* is the fluid which lubricates the surfaces of joints. It contains, according to Mr Hatchett,* a small portion of phosphate of lime, and of phosphate of soda and ammonia; the animal principle appeared to be albumen. Synovia.

2148. *Pus* is a term applied to a variety of secretions from abscesses and ulcerated surfaces. When it indicates a healing sore, it has been called *healthy pus*, and has the following properties. It has the consistency of cream, a yellowish colour, and exhibits, under the microscope, the appearance of globules diffused through a fluid.† Its specific gravity is about 1,030. It does not affect vegetable colours till it has been some time exposed to air, when it becomes slightly sour; it does not easily mix with water, alcohol, or dilute acids.‡ Pus.

2149. *Formic acid*, or acid of ants. This is a peculiar acid which exists in the red ant; it was examined by Fourcroy and Vauquelin who inferred that it is merely a mixture of acetic and malic acids. Dobereiner has formed it artificially, by slightly heating bi-tartrate of potassa or tartaric acid with black oxide of manganese. A great quantity of carbonic acid escapes, and a sour colourless liquid distils, which is formic acid. It may be obtained from red ants by infusing them in warm water and distillation. It is regarded as a secretion and as constituted of Formic acid.

| | Atoms. | | |
|--------------------|-------------|----------|--------------|
| Oxygen | 2 | 12 | Composition. |
| Carbon | 3 | 24 | |
| Hydrogen | 1 | 1 | |
| | | <hr/> 37 | |

Or as constituted of 1 volume of the vapour of water + 2 volumes of carbonic oxide gas.§ Its compounds are termed *Formiates*.

SECTION VI. *Urine, Urinary Calculi, &c.*

2150. This secretion presents, perhaps, greater difficulties to the analytical chemist, than any other animal product; it is extremely complex, and subject to constant change in the propor- Urine.

* *Phil. Trans.* 1799.

† Home, *On Ulcers*. 2 Edit. p. 13.

‡ See Dr Pearson's *Experiments on Pus*, Nicholson's *Journal*, xxx.

§ *Ann. of Philos.* N. S. ix. 490.

tions of its components, and in disease several new substances make their appearance.

The chemical history of the urine is of the utmost importance to the medical practitioner; it teaches the nature of the substances which occasionally predominate, so as to constitute *gravel* and *calculi*: and shows the means of influencing and modifying its composition.

The general characters of the urine are too well known to need description. Its specific gravity is of course liable to much variation even in the healthy state, fluctuating between 1005 and 1040. The average is about 1020.

Substances
found in it.

2151. The substances that are always found in urine are, according to Mr Brande's experiments, the following:

- | | |
|--------------------------|---------------------------|
| 1. Water. | 7. Phosphate of soda. |
| 2. Carbonic acid. | 8. Phosphate of magnesia. |
| 3. Phosphoric acid. | 9. Common salt. |
| 4. Uric acid. | 10. Sulphate of soda. |
| 5. Phosphate of lime. | 11. Albumen. |
| 6. Phosphate of ammonia. | 12. Urea.* |

2152. The existence of free acid in recently voided urine is easily demonstrated by its property of reddening vegetable blues, and it performs the important office of retaining some difficultly soluble salts in permanent solution; so that whenever this natural acidity is diminished, the urine has a tendency to deposit the earthy phosphates.†

Carbonic
acid.

2153. The presence of *carbonic acid* may be shown by placing urine under the receiver of the air-pump; during exhaustion it escapes, sometimes copiously, but at other times in minute quantities only.

Phosphoric
acid.

2154. The free *Phosphoric acid* may be shown by the addition of carbonate of lime, a portion of which is converted into phosphate of lime.

Uric acid,

2155. *Uric acid* is one of the peculiar characteristics of the urine; its presence may be shown by evaporating urine to half its bulk, which produces a precipitate consisting of phosphate of lime and uric acid; the former may be dissolved by dilute muriatic acid, which leaves the latter in the form of a reddish powder. This acid has been very ably examined by Dr Henry, who made it the subject of a thesis published in 1807: Dr

* According to Berzelius 1000 parts of urine are composed of

| | |
|--|--------|
| Water | 933,00 |
| Urea | 30,10 |
| Uric acid | 1,00 |
| Free lactic acid, lactate of ammonia, and animal matter not separable from them | 17,14 |
| Mucus of the bladder | 0,32 |
| Sulphate of potassa | 3,71 |
| " of soda | 3,16 |
| Phosphate of soda | 2,94 |
| " of ammonia | 1,65 |
| Muriate of soda | 4,45 |
| " of ammonia | 1,50 |
| Earthy matters, with a trace of fluete of lime | 1,00 |
| Siliceous earth | 0,03 |

† Dr Prout maintains that the acidity of recent urine is occasioned by super-salts, and not by uncombined acid.

Prout has also given much valuable information in relation to it.

Uric acid, called sometimes lithic acid, as constituting the principal ingredient in certain urinary calculi, may be abundantly obtained by digesting such calculi (2169) in caustic potassa, filtering the solution, and adding excess of muriatic acid, which causes a precipitate of uric acid, which is to be washed with warm water, and dried.

Uric acid, thus obtained, is a grey powder, of scarcely any taste, and requiring according to Dr Henry 1720 parts of water at 60°, and 1150 parts at 212° for solution. It reddens infusion of litmus, and readily dissolves in caustic potassa, and soda; it is sparingly soluble in ammonia, and insoluble in the alkaline carbonates.

According to Dr Prout, uric acid requires at least 10000 parts of water at 60° for its solution, but urate of ammonia requires only about 480 times its weight at the same temperature, and affords a precipitate of uric acid, on the addition of any other acid; for these, among other reasons, Dr Prout regards urate of ammonia, and not pure uric acid, as existing in urine.

2156. Uric acid dissolves in nitric acid, and upon evaporation a residuum of a fine red tint is obtained, which is peculiar to this combination, and which Dr Prout has lately shown to possess distinct acid properties; he has called it *purpuric acid*.*

2157. When uric acid is submitted to destructive distillation, it affords carbonate of ammonia, and a peculiar compound, which sublimes in crystals, and which, according to Dr Henry, consists of a peculiar acid united to ammonia; a quantity of charcoal remains in the retort. Its ultimate constituents, according to Dr Prout, are

| | | | |
|---|--------------------------|---------|-----|
| 1 | proportional of nitrogen | . . . | 14 |
| 2 | ———— carbon | 6 × 2 = | 12 |
| 1 | ———— oxygen | . . . | 8 |
| 4 | ———— hydrogen | . . . | 1 |
| | | | — |
| | | | 35† |

2158. *Phosphate of Lime* may be precipitated from urine by the addition of ammonia; its relative quantity is liable to much fluctuation; sometimes it becomes so great as to be deposited as the urine cools, constituting what has been termed *white sand*.

2159. The *Phosphates of Ammonia*, of *Soda*, and of *Magnesia*, and *common Salt*, constitute the principal crystallizable salts contained in the urine; the first of these is probably in great part produced during evaporation, for the saline mass obtained by inspissating urine is no longer acid; the carbonic

* *Phil. Trans.* 1818.
† The *urates* have principally been examined by Dr Henry, and an account of many of them is given in his *Thesis* above quoted.

having escaped, and the phosphoric being saturated by ammonia. The *microcosmic salt*, or *fusible salt of urine*, of the old chemists, is chiefly phosphate of ammonia with a little phosphate of soda, or perhaps a triple *ammonio-phosphate of soda*. (1049).

Ammoniaco-
magnesian
phosphate.

2160. The *Ammoniaco-magnesian Phosphate* (1190) is a common, and almost constant ingredient in urine. It forms a part of the white sand voided in certain calculous affections, and is sometimes formed in a film upon the surface of the urine, having been held in solution by carbonic acid, and being deposited as that gas escapes.

Sulphuric
acid.

2161. The existence of *Sulphuric acid*, probably combined with *soda*, and perhaps also with *potassa*, may be detected in urine by the addition of nitrate of baryta, which occasions a precipitate of sulphate of baryta.

Albuminous
matter.

As urine blackens silver, it has been said to contain *sulphur*; but this is not the case with recent urine, and when it becomes slightly putrid it evolves a little sulphuretted hydrogen.

2162. The existence of *albuminous matter* in urine is sometimes easily demonstrated; at others, the secretion seems not to contain it. It has been said, by Mr Cruickshank, that the urine in some dropsical cases contains so much albumen as to be coagulable by heat,* but if that ever be the case, the secretion could hardly be called urine. It seems questionable whether the albumen of urine should not sometimes be regarded as derived from the mucous secretion of the bladder. Dr Prout, in his *Inquiry into the Nature and Treatment of Gravel*, &c. has described some cases of albuminous urine, and has adverted to its method of cure.

Urea

2163. *Urea* is the principle which confers upon urine its chief peculiarities.

It may be obtained by slowly evaporating urine to the consistency of sirup; on cooling it concretes into a saline mass, which by digestion in alcohol, furnishes urea. By carefully distilling off the alcohol, the urea remains in the form of a brown crystallized mass, which, by purification, furnishes colourless prismatic crystals.†

Properties.

Urea is very soluble; water, at 60°, takes up about its own weight, and boiling water appears to dissolve it in any quantity, and without alteration: boiling alcohol takes up its own weight, and on cooling the urea separates in crystals. Sulphuric ether scarcely dissolves an appreciable portion. Nitric acid produces a crystalline precipitate in the aqueous solution of urea consisting of the two substances according to Dr Prout, in the following proportions:

| | |
|-----------------------|--------------|
| Nitric acid | 47,37 |
| Urea | 52,63 |
| | <hr/> 100,00 |

* *Phil. Mag.* vol. ii.

† Other processes have been given for obtaining urea, which are objectionable, on account of their complexity; indeed it is doubtful whether, by the action of heat and alcohol, as above described, it is not considerably altered.

A very similar compound may also be produced with oxalic acid.

The fixed alkalies decompose urea, and occasion the evolution of ammonia and some other products. It is to this substance that the copious production of volatile alkali, during the destructive distillation of urine, is referable ; and the ammonia which is found in combination with the acids, in putrid urine, is derived from the same source.

Urea combines with most of the metallic oxides ; with oxide of silver the compound is grey, and it decomposes with detonation when heated.*

In some diseased states of the urine there is a morbid excess of urea, which may be detected by putting a little of the urine into a watch-glass, and carefully adding an equal quantity of nitric acid, in such a manner that the acid shall subside to the lower part of the glass ; if spontaneous crystallization take place it indicates excess of urea.†

2164. Such are the properties of the principal ingredients in human urine, to which several others have been added by different chemists ; but their existence is only occasional, and often doubtful.

2165. The urine suffers some very remarkable changes in certain diseases, which have been but superficially inquired into by chemists. In cases of injury of the spine, affecting the nerves that supply the kidneys ; the urine is always turbid, and often alkaline ; and there is a considerable tendency in these cases to form calculi.

Effect of diseases.

* M. Wöhler has stated that when cyanogen was made to act upon liquid ammonia, amongst other products were oxalic acid and a white crystalline substance ; the latter appeared to be formed also whenever cyanic acid was combined with ammonia by double decomposition ; it is obtained most readily when cyanate of silver is decomposed by muriate of ammonia, or cyanate of lead by pure ammonia. The substance obtained appeared in colourless, transparent four-sided rectangular crystals. It is unlike the other cyanates in not evolving carbonic and cyanic acids by the action of other acids, nor does it precipitate the salts of lead and silver.

Artificial formation of Urea.

When nitric acid is added to it, brilliant scaly crystals are formed, which, when purified are very acid ; these being neutralized give nothing but nitrates and the peculiar matter in its original state.

This peculiar action with nitric acid, induced a comparison of it with urea obtained from urine, when the latter body was found to be identical with the peculiar crystalline substance or cyanate of ammonia, in all the properties attributed to the former body by Proust and others. M. Wöhler remarked a circumstance in addition to those which have been pointed out relative to urea, namely, that when either it or the artificial compound is decomposed by heat, besides a large quantity of carbonate of ammonia, there is produced, towards the end of the operation, the odour of cyanic acid, resembling that of acetic acid, exactly as in the distillation of the cyanate of mercury, or uric acid, or urate of mercury.

If urea is formed by the union of cyanic acid and ammonia, the composition of the former ought to agree with that of the latter. The cyanate of ammonia is composed of 56,92 cyanic acid 28,14 ammonia and 14,74 of water ; so that the ultimate composition of this salt and of the urea, as analyzed by Dr Prout, are as follows :

| | Cyanate of ammo. | | | | Urea. | | | |
|----------|------------------|---|---------|-------|-------|---|---------|--------|
| Azote | - | - | 4 atoms | 46,78 | - | - | 4 atoms | 46,650 |
| Carbon | - | - | 2 " | 20,19 | - | - | 2 " | 19,975 |
| Hydrogen | - | - | 8 " | 6,59 | - | - | 8 " | 6,670 |
| Oxygen | - | - | 2 " | 26,24 | - | - | 2 " | 26,650 |
| | | | | 99,80 | | | | 99,945 |

Ann. de Chim. xxxvii. 330.

† Prout, on Gravel, &c. p. 10.

Diabetes.

In the disease called *diabetes*, the urine is not only secreted in excess, but often contains a substance of a sweet taste, having the properties of sugar, and its specific gravity is considerably above the healthy standard.*

2166. The urine of graminivorous animals differs considerably from that of the human subject. Carbonates, muriates, and phosphates, are the leading ingredients; it also contains urea, but not uric acid; potassa is usually the predominating alkali.

Sand.

2167. It frequently happens, from a variety of causes, that certain ingredients of human urine are secreted in excess, and deposited in a solid form, constituting *sand*, or *gravel* and *calculi*.

Sand is either *white* or *red*; the former consists of phosphate of lime, and ammoniaco-magnesian phosphate, either separate or mixed, and the latter is chiefly uric acid. The former deposition is prevented by the use of acids, and the latter by alkalies and the alkaline earths. The modes of exhibiting these remedies, and the effects which they produce, are described in a paper printed in the *Quarterly Journal of Science and Arts*, vol. vi.

Calculi.

2168. Urinary calculi are, for the most part, composed of materials that exist at all times in the urine, though there are a few substances that only make their occasional appearance in them. The following are their component ingredients:

Components.

- | | |
|---------------------------------|-----------------------|
| 1. Uric acid. | 5. Oxalate of lime. |
| 2. Urate of ammonia. | 6. Carbonate of lime. |
| 3. Phosphate of lime. | 7. Cystic oxide. |
| 4. Ammonio-magnesian phosphate. | |

Uric acid calculus.

2169. The calculi composed of uric acid, of which the chemical properties have already been described (2155), are of a brown or fawn-colour; and, when cut through, appear of a more or less distinctly laminated texture. Their surface is generally smooth, or nearly so, being sometimes slightly tuberculated. Before the blow-pipe this calculus blackens, and gives out a peculiar ammoniacal odour, leaving a minute portion of white ash: it is soluble in solution of pure potassa, and heated with a little nitric acid, affords the fine pink compound, above mentioned (2156).

Phosphate of lime calculus.

2170. Phosphate of lime calculus is of a pale brown, or grey colour, smooth, and made up of regular and easily separable laminæ. It is easily soluble in muriatic acid and precipitated by pure ammonia, and does not fuse before the blow-pipe. *Calculi from the prostate gland*, are always composed of phosphate of lime.

Triple calculus.

2171. The ammonio-magnesian, or triple calculus, is generally white, or pale grey, and the surface often presents minute crystals; its texture is generally compact, and often somewhat hard and translucent; heated violently by the blow-pipe, it exhales ammonia, and leaves phosphate of magnesia. It is

* Henry on Diabetic Urine. *Medico-Chirurgical Trans.* vol. ii. p. 118.

more easily soluble than the preceding, and oxalate of ammonia forms no precipitate in its muriatic solution.

2172. It frequently happens that calculi consist of a mixture of the two last-mentioned substances, in which case they melt before the blow-pipe, and are hence termed *fusible calculi*. They are white or nearly so, and softer than the separate substances, often resembling chalk in appearance. They are easily soluble in muriatic acid, and if oxalate of ammonia be added to their solution, the lime is precipitated in the state of oxalate. Fusible calculus.

2173. Oxalate of lime forms calculi, the exterior colour of which is generally dark brown, or reddish; they are commonly rough, or tuberculated upon the surface, and have hence been called *mulberry calculi*. Before the blow-pipe they blacken and swell, leaving a white infusible residue, which is easily recognised as quicklime (1955). Small oxalate of lime calculi are, however, sometimes perfectly smooth upon the surface, and much resemble a hemp-seed in appearance. Urate of ammonia.

2174. Urate of ammonia is admitted by Mr Brande among urinary calculi, upon the authority of Dr Prout.* Its surface is sometimes smooth, sometimes tuberculated; it is made up of concentric layers, and its fracture is fine earthy, resembling that of compact lime-stone; it is generally of a small size, and rather uncommon, though it often occurs mixed with uric acid. It usually decrepitates before the blow-pipe, is more soluble than the uric calculus, evolves ammonia when heated with solution of potassa, and is readily soluble in the alkaline carbonates, which pure uric acid is not.

2175. Dr Prout and Mr Smith† have described calculi composed almost entirely of carbonate of lime, but this species is exceedingly rare.

2176. Cystic oxide is a peculiar animal substance; the calculi composed of it, which are rare, are in appearance most like those of the ammonio-magnesian phosphate. They are soft, and when burned by the blow-pipe, exhale a peculiar fetid odour. They are soluble in nitric, sulphuric, muriatic, phosphoric, and oxalic acids, and also in alkaline solutions. Cystic oxide.

2177. The substances which have been described, with the exception of cystic oxide, are sometimes intimately blended in calculi; sometimes they form alternating layers; and in a few cases four distinct layers have been observed, the nucleus being uric, upon which the oxalate, and phosphate of lime, and the triple phosphate, are distinctly and separately arranged.

2178. Dr Marcet has described a calculus composed of a peculiar animal matter, which he calls *Xanthic Oxide*, from its property of giving a yellow colour when acted on by nitric acid: he has also announced the existence of calculus composed of *fibrine*.‡ Xanthic oxide.

* Phil. Trans. 1808.

† Med. et Chir. Trans. xi 14.

‡ Essay on Calculous Disorders, 2d edit. p. 103.

2179. These are the principal chemical facts belonging to the history of urinary calculi. In Dr Wollaston's and Mr Brande's valuable papers upon this subject* much additional information will be found.†

SECTION VII. *Cutis, or Skin, Membrane, &c.*

2180. The skin of animals consists of an exterior albuminous covering, or *cuticle*, under which is a thin stratum of a peculiar substance, called by anatomists *rete mucosum*, and which lies immediately upon the *cutis*, or true skin, of which the principal component is *gelatine*.

Gelatine.

2181. The following are the chemical properties of pure gelatine. It is colourless, semi-transparent, and nearly tasteless. It is softened by long continued immersion in cold water: in hot water it readily dissolves, and forms a solution of a slightly milky appearance, which, if sufficiently concentrated, concretes on cooling into the tremulous mass usually called *jelly*, and which is easily soluble in cold water; when dried in a gentle heat it acquires its original appearance, and is as soluble as before. When dry, gelatine undergoes no change, but its solution soon becomes mouldy and putrescent. Submitted to the action of heat it affords the usual products of animal substances.‡

Action of tannin.

It is readily soluble in diluted acids and alkaline solutions, and forms no soap with the latter. Its aqueous solution is not affected by solution of corrosive sublimate, and few of the metallic salts occasion any precipitate in it. Chlorine passed through its solution, occasions a white elastic matter to separate, which is not soluble in water, and which in some properties resembles albumen. It is insoluble in alcohol and ether. Solution of tannin occasions a white precipitate in solution of gelatine; and hence, vegetable astringents such as galls or catechu, are generally employed as tests for its presence. But as tannin precipitates albumen, it cannot be relied on as an unequivocal test, unless we previously ascertain the non-existence of albumen by corrosive sublimate.§||

Sulphate of platinum a test of gelatine.

Mr E. Davy recommends sulphate of platinum as a very delicate test of gelatine, with which it forms a brown insoluble compound, in solutions too weak to be affected by vegetable astringents.||

Action of sulphuric acid.

2182. The action of sulphuric acid upon gelatine has been investigated by M. Braconnot. Twelve parts of powdered glue

* *Phil. Trans.* 1797 and 1810.

† Dr Marcet and Dr Prout have published excellent dissertations on *Calculous Disorders*, containing all that is most important upon the subject.

‡ Hatchett, *Phil. Trans.* vol. xc

§ Bostock. *Nicholson's Journal*, xiv. and xxi.

|| *Phil. Trans.* 1820, p. 119.

and 24 of sulphuric acid, were left together for 24 hours; about 60 parts of water were then added, and the whole boiled for 5 hours, adding water at intervals; the solution was then saturated with chalk, filtered, and suffered to evaporate spontaneously. In a month crystals were deposited, which, being purified by solution and a second crystallization, much resembled sugar of milk, though they differ from that substance in affording a peculiar acid, called by M. Braconnot *Nitro-saccharine acid*, when acted upon by nitric acid.*

2183. The different kinds of gelatine differ considerably in viscosity. Mr Hatchett has remarked that the gelatine obtained from skins possesses a degree of viscosity inversely as their softness or flexibility; the most adhesive kinds of gelatine, too, are less easily soluble in water than those which are less tenacious. The principal varieties of gelatine in common use are,

a. Glue, which is prepared from the clippings of hides, hoofs, &c., obtained at the tan-yard; these are first washed in lime-water, and afterwards boiled and skimmed; the whole is then strained through baskets, and gently evaporated to a due consistency; afterwards it is cooled in wooden moulds, cut into slices, and dried upon coarse net-work. Good glue is of a semi-transparent and deep brown colour, and free from clouds and spots. When used it should be broken into pieces, and steeped for about 24 hours in cold water, by which it softens and swells; the soaked pieces may then be melted over a gentle fire, or in a water-bath, and in that state applied to the wood by a stiff brush. Glue will not harden in a freezing temperature, the stiffening depending on the evaporation of its superfluous water. Glue.

b. Size is less adhesive than glue, and is obtained from parchment shavings, fish-skin, and several animal membranes. It is employed by book-binders, paper-hangers, and painters in distemper, and is sometimes mixed with flour, gum, &c. Size.

c. Isinglass is prepared from certain parts of the entrails of several fish; the best is derived from the sturgeon, and is almost exclusively prepared in Russia. It should be free from taste and smell, and entirely soluble in warm water, which is seldom the case, in consequence of the presence of some albuminous parts. When the jelly of isinglass is concentrated by evaporation and carefully dried, it forms a very choice kind of glue.† Isinglass.

2184. *Leather* is a compound of gelatine and vegetable astringent matter, formed by steeping the skins of animals in the infusions of certain barks. The skins are previously prepared by soaking in lime-water, which renders the cuticle and hair easily separable, and are afterwards softened by allowing them to enter into a degree of putrefaction. In this state they are submitted to the action of infusion of oak-bark, or other Leather.

* Ann. de Chim. et Phys. xiii.

† Aikin's Dictionary, Art. Gelatine.

astringent vegetable matter (1837), the strength of which is gradually increased until a complete combination has taken place, which is known by the leather being of an uniform brown colour throughout; whereas, in imperfectly tanned leather a white streak is perceptible in the centre.

Tawed leather is made by impregnating the skin duly prepared, with a solution of alum and common salt; it is afterwards trodden in a mixture of yolk of eggs and water.

Curried
leather.

Curried leather is made by besmearing the skin, or leather, while yet moist, with common oil, which, as the humidity evaporates, penetrates into the pores of the skin, giving it a peculiar suppleness, and making it, to a considerable extent, water-proof. As familiar examples of these processes, the thick sole-leather for shoes and boots is *tanned*; the upper-leather is *tanned* and *curried*; the white leather for gloves is *tawed*; and fine Turkey-leather is *tawed*, and afterwards slightly *tanned*.*

2185. The different *membranes* of the body, and the *tendons*, are chiefly composed of gelatine, for by long digestion in warm water they gradually soften, and become ultimately almost perfectly soluble.

SECTION VIII. *Muscle, Ligaments, Horn, Hair, &c.*

2186. When the *muscular parts* of animals are washed repeatedly in cold water, the fibrous matter which remains consists chiefly of albumen, and is in its chemical properties analogous to the clot of blood. Muscles also yield a portion of gelatine; and the flesh of beef, and some other parts of animals, afford a peculiar substance of an aromatic flavour, called by Thenard, *osmazome*.

Osmazome.

2187. 30 parts of beef fibre, acted on by as much sulphuric acid, yielded M. Braconnot, a portion of fat, and on diluting the acid mixture, and saturating with chalk, filtering and evaporating, a substance, tasting like osmazome was obtained, which was often boiled in different portions of alcohol: the alcoholic solutions, on cooling, deposited a peculiar white pulverulent matter, which Braconnot calls *leucine*, and which acted upon by nitric acid affords a crystallizable *nitroleucic acid*.†

Leucine.

2188. *Ligaments, horn, nail, and feathers*, consist principally of albumen.

Hair.

2189. *Hair* consists principally of a substance, having the properties of coagulated albumen. It also contains gelatine, and the soft kinds of hair yield it more readily than those which are harsh, strong, and elastic.‡

Vauquelin discovered in hair two kinds of oil; the one white, and existing in all hair; the other coloured, yellow from

* Aikin's *Dict* Article *Leather*.

‡ Hatchett, *Phil. Trans.* 1800.

† *Ann. de Chimie et Phys.* xiii. p. 118.

red hair, and dark coloured when obtained from dark hair. Black hair also contains iron and sulphur. He supposes that where hair has become suddenly grey, the effect is produced by the evolution of acid matter, which has destroyed the colour of the oil.

2190. *Feathers, quills, and wool*, are also possessed of the properties of albumen, and appear to contain no gelatine. Feathers, &c.

SECTION IX. Fat, Spermaceti, &c.

2191. The fat of animals, when freed by fusion or pressure from cellular membrane, is of various degrees of consistency, as seen in *tallow, lard, and oil*. When pure, it has little taste or smell, but it acquires both by keeping, and becomes rancid and slightly sour. The softer varieties fuse at about 90° , and the harder at 120° . Decomposed at a red heat, they afford abundance of olefiant gas, and a small portion of charcoal; products analogous to those of vegetable oil. (765.) When burned, they produce water and carbonic acid, containing the same ultimate elements, in the same proportions as vegetable oils. (1880). Tallow, lard, and oil.

They also produce soaps by combination with alkalies.

Nitric acid, heated in small quantity with any of the fatty substances, renders them harder, and considerably increases their solubility in alcohol. Among the vegetable oils this change is most remarkably produced upon cocoa-nut, and castor-oils, the latter becoming converted into a solid matter, which, when cleansed of adhering acid by washing, resembles soft wax. Action of nitric acid.

2192. The experiments of Braconnot and Chevreul, already quoted, (1870) have shown that the different kinds of oil and fat contain two substances, to which they have given the names *stearine* and *elaine*, the former solid, the latter liquid at common temperatures. The table below shows their relative proportions in different fats and oils:*

These principles may be obtained by boiling hogs' lard in alcohol; the fluid, on cooling, deposits a crystalline matter, which is to be purified by a second solution and crystallization; it is then pure *stearine*, white, brittle, tasteless, and inodorous; it fuses at a little below 120° , and forms soap with alkalies.

When the alcohol which has deposited the whole of the stearine is distilled, an oily liquid remains, which is *elaine*. It is fluid at 58° ; it generally is of a yellow colour, and is convertible into soap.

| | Elaine. | Stearine. | | Elaine. | Stearine. |
|--------------------------|---------|-----------|--------------|---------|-----------|
| * Butter, made in summer | 60 | 40 | Goose-fat | 68 | 32 |
| Ditto, winter | 37 | 63 | Ducks'-fat | 72 | 28 |
| Hogs'-lard | 62 | 38 | Turkey's-fat | 74 | 26 |
| Beef-marrow | 24 | 76 | Olive-oil | 72 | 28 |
| Mutton ditto | 74 | 26 | Almond-oil | 76 | 24 |

Margaritic
acid.

2193. When soap composed of hogs'-lard and potassa, is put into water, a portion only is dissolved, the remainder consists of white scales, composed of the alkali united to a peculiar acid, called by Chevreul, from its pearly appearance, *margaritic acid*, and separable from the above combination by muriatic acid.

It is insoluble in water, tasteless, fusible at 134° , and crystallizes on cooling in brilliant white needles. It is soluble in alcohol. It unites with potassa in two proportions, the one compound containing 100 acid + 8,80 potassa; the other, 100 acid + 17,77 potassa. These compounds have been termed *margarates of potassa*.

Oleic acid.

2194. The portion of the hogs'-lard soap soluble in water, consists of another peculiar substance united to potassa, which Chevreul has called *oleic acid*. It may be obtained from its solution by tartaric acid, which causes it to separate in the form of an oily matter, that is to be again united to potassa, and separated as before. This substance solidifies at about 40° , and it forms compounds, called *oleates*. It appears probable that, by the action of alkalies, the stearine is converted into what Chevreul has termed margaric acid, and the elaine into oleic acid.*†

Spermaceti.

2195. *Spermaceti* or *Cetine* is a peculiar matter, which concretes from the oil of the *spermaceti whale*. It fuses at 112° , and at higher temperatures is volatile, but if repeatedly distilled it loses its solid form, and becomes a liquid oil. It is soluble in boiling alcohol, and abundantly so in ether. It forms a soap with potassa, which yields, on decomposition, a substance called by Chevreul, *cetic acid*.‡

2196. In the *yolk of eggs* there is a considerable quantity of oily matter, which may be obtained by pressure after boiling; it is yellow and tasteless.

Ambergris.

2197. *Ambergris*, which is a concretion from the intestines of the spermaceti whale, also contains a considerable portion of fatty matter, amounting in some specimens to 60 *per cent*. It is only found in the unhealthy animal.§ Its chief constituent is a substance very analogous to cholesterine, and to which Pelletier and Caventou have given the name of *ambreine*. By digestion in nitric acid, ambreine is converted into a peculiar acid called the *ambreic acid*.||

* *Annales de Chimie*, xciv. The experiments of Bussy and Lecanu show that fat treated with nitric acid is partly converted into oleic and margaric acids. as analogy of composition admits extending these results to all bodies formed of stearine and oleine, it will be observed that the property of converting these bodies into oleic and margaric acids, which, for a long time, was limited to the action of the alkalies only, then observed in sulphuric acid, in oxygen and in heat, is also found to exist in nitric acid.—*Jour. de Pharm.* Nov. 1826, and *Ann. Philos.* N. S. 2, 145.

† By mixing 1 volume of carbonic acid with 10 of carburetted hydrogen, and 30 of hydrogen, and passing the mixture through a red-hot porcelain tube, Berard is said to have produced a substance in small white crystals, having many of the properties of fat—Thomson's *Annals*, xii.

‡ *Annales de Chimie*, xc.

§ Home's *Lectures on Comparative Anatomy*, vol. i. p. 470.

|| *Ann. Philos.* xvi.

SECTION X. *Cerebral Substance.*

2198. According to Vauquelin, the *cerebral substance* consists of

| | |
|-------------------------------------|-------|
| Water | 80,00 |
| White fatty matter | 4,53 |
| Red fatty matter | 0,70 |
| Albumen | 7,00 |
| Osmazome | 1,12 |
| Phosphorus | 1,50 |
| Acids, salts, and sulphur | 5,15 |

100.

The *pulp of nerves* seems to be of a similar nature.*

2199. The brain of animals, when boiled in alcohol, furnishes a peculiar fatty matter, which the solution deposits as it cools, in brilliant scales. It requires a higher temperature than that of boiling water for its fusion, and appears in many respects analogous to cholesterine. (2137.) The same substance is often seen in the alcohol employed to preserve anatomical preparations of the brain and nerves.

SECTION XI. *Shell and Bone.*

2200. We are indebted to Mr Hatchett for two excellent dissertations on the chemical properties of these parts of animals, published in the *Philosophical Transactions* for 1799 and 1800.

He has divided *shells* into two classes; the texture of the first is compact, brittle, and resembling porcelain; their surface is smooth, and they are often beautifully variegated. When exposed to a red heat they crackle, and lose the colour of their enamelled surface, emitting scarcely any smoke or smell. They dissolve in dilute muriatic acid with copious effervescence, and form a transparent solution, in which neither pure ammonia nor acetate of lead produce any precipitate, but carbonate of ammonia throws down carbonate of lime. Hence these, which are called *porcellaneous shells*, may be considered as composed of carbonate of lime, united to a very small portion of gelatine: most of the univalve shells, such as whelks, limpets, cowries, and many of the beautiful convoluted shells of tropical countries, belong to this class.

Porcellaneous shells.

2201. The second class, or *mother-of-pearl shells*, are tougher, glossy, and iridescent; they are mostly bivalves, and all the oyster and muscle species belong to it. When heated, they exhale smoke and the smell of burned horn; immersed in

Mother-of-pearl shells.

* Thomson's *System*, vol. iv. p. 482.

muriatic acid, they only partially dissolve, and leave a series of cartilaginous layers, and an outer epidermis. Each membrane appears to have a corresponding stratum of carbonate of lime, the solution indicating no trace of any phosphate. The animal part is in some cases, as in mother-of-pearl, tough and indurated, and when dried becomes exactly like horn; in other instances, as in the bone of cuttle fish, it appears in the form of delicate and tender membrane.

In both classes of shells, therefore, the hardening principle is carbonate of lime; in porcellaneous shells there is very little animal matter which is gelatine; and in mother-of-pearl shells, it is albumen, and in larger quantities.

Pearls. 2202. *Pearls* are exactly similar in composition to what is termed *mother-of-pearl*, in which Mr Hatchett found

| | |
|-----------------------------|----|
| Carbonate of lime | 66 |
| Albumen | 24 |

Scales of fish. 2203. In the *scales of fish*, and in the *crusts* of lobsters, crabs, prawns, and cray-fish, Mr Hatchett found the animal portion to consist of cartilage; the hardening part was a mixture of carbonate and phosphate of lime. From *lobster-shell* Merat-Gulliot obtained

| | |
|-----------------------------|-------|
| Carbonate of lime | 60 |
| Phosphate of lime | 14 |
| Cartilage | 26 |
| | <hr/> |
| | 100 |

Vauquelin obtained from 100 parts of *hen's egg shell*

| | |
|-----------------------------|-------|
| Carbonate of lime | 89,6 |
| Phosphate of lime | 5,7 |
| Animal matter | 4,7 |
| | <hr/> |
| | 100 |

Zoophytes 2204. *Zoophytes*, according to Mr Hatchett's researches, may be divided into four classes; the first resemble porcellaneous shells, and consist entirely of carbonate of lime, with a very minute quantity of gelatinous matter; of this the common white coral (*madrepora virginea*) is an example. The second consist of carbonate of lime, and a cartilaginous substance, and are therefore analogous to mother-of-pearl shell; to this class belong the *madrepora ramea*, and *madrepora fascicularis*. The third class is composed of a cartilaginous matter, with carbonate and phosphate of lime; to this belongs the red coral (*gorgonia nobilis*). The fourth class contains sponges, composed almost entirely of albuminous matter.*

Bone and Ivory. 2205. *Bone*, and *Ivory*, like the preceding substances, is essentially composed of soft and hard parts. When ground bone is digested in warm water, a portion of fat is first separated, and by long-continued ebullition, a solution which gelatinizes on cooling is obtained. If fresh bone be immersed in diluted

* Phil. Trans. 1800.

muriatic acid, the fat, gelatine, and hardening matter are dissolved, and a kind of skeleton of the bone remains in the form of a cartilaginous substance, which when dried exactly resembles horn. It appears, therefore, that the soft parts of bone are, *fat, gelatine, and albumen.*

The earthy salts, which constitute the hardening principle of bone, are phosphate and carbonate of lime, with a minute quantity of sulphate of lime, and traces of phosphate of magnesia. Fourcroy and Vauquelin obtained from ox-bones,

Earthy salts, &c.

| | |
|---------------------------------|-------|
| Animal matter | 51 |
| Phosphate of lime | 37,7 |
| Carbonate of lime | 10 |
| Phosphate of magnesia | 1,3 |
| | <hr/> |
| | 100 |

2206. The *enamel of teeth* is perfectly destitute of cartilage, and consists chiefly of phosphate of lime and a portion of gelatine. Mr Pepys found its component parts

Enamel of teeth.

| | |
|-----------------------------|-------|
| Phosphate of lime | 78 |
| Carbonate of lime | 6 |
| Gelatine | 16 |
| | <hr/> |
| | 100 |

The same chemist has given the following as the composition of the teeth.*

| | Roots of the teeth. | Teeth of Adults. | First Teeth of Children. |
|---------------------|------------------------|---------------------|-----------------------------|
| Phosphate of lime | 58 | 64 | 62 |
| Carbonate of lime | 4 | 6 | 6 |
| Cartilage | 28 | 20 | 20 |
| Loss | 10 | 10 | 12 |
| | <hr/> | <hr/> | <hr/> |
| | 100 | 100 | 100 |

2207. When bones are submitted to destructive distillation, the gelatine and albumen which they contain are abundantly productive of ammonia; water, and carbonic acid are also formed and a portion of highly fetid empyreumatic oil. There remains in the vessel a quantity of charcoal mixed with the earthy substances, which is, in that state, called *ivory black*. It is employed as the basis of some black paints and varnishes.

Destructive distillation of bones.

SECTION XII. Of Animal Functions.

2208. Chemistry has hitherto done little towards elucidating the functions of animals, and it is scarcely possible to describe the little that has been done, without such frequent reference to anatomical and physiological inquiries as would be irrelevant to the present work; we shall, therefore, only enumerate the

* Fox, on the Teeth.

principal chemical phænomena that have been experimentally illustrated, in relation to this subject.

Digestion.

2209. *Digestion* is a process by which the food of animals is converted into chyle, and which in conjunction with *respiration*, tends to the production of blood. The mechanism by which it is carried on differs considerably in the different classes of animals; the present remarks will relate chiefly to man, and to the carnivorous tribe.

Chyme.

The food, duly masticated in the mouth, and blended with a considerable portion of saliva, is propelled into the stomach, where it soon undergoes a remarkable change, and, in the course of a few hours, is converted into an apparently homogeneous pulpy mass, which has been termed *chyme*, and which has little or no resemblance to the original food. This very curious change is only referable to the operation of a secretion peculiar to certain glands of the stomach; it has been termed *gastric juice*, and all that is known respecting it is, that it has very energetic solvent powers, in regard to the greater number of animal and vegetable bodies; the remarkable property of living substances to resist its action is curiously illustrated by the circumstance that the stomach itself, after death, is occasionally eaten into holes by its action; it instantly coagulates all albuminous substances, and afterwards softens and dissolves the coagulum. There are some substances that remarkably resist its action, such as the husk of grain, and of many seeds, which, if not previously broken by mastication, pass through the stomach and bowels nearly unaltered. It is hardly worth while to detail the experiments that have been undertaken on the gastric juice, since they are much at variance, and it is impossible to say whether the secretion has ever been examined in a state even approaching to purity. It has been described as a glairy fluid, of a saline taste; sometimes it is said to be acid, and sometimes bitter; but no light whatever has been thrown by any of these researches upon the cause of its singular solvent energies.

Gastric juice.

Absorption
from the
stomach.

It has sometimes been matter of surprise, that although animals drink copiously with their food, the consistency of the chyme is not affected by it, and by the time that it reaches the right, or pyloric extremity of the stomach, the liquid has disappeared. Sir Everard Home's curious physiological researches have shown that liquids are copiously and rapidly removed by absorbents belonging principally to the left, or cardiac portion of the stomach, and that during digestion there is an imperfect division of the stomach into two cavities, by the contraction of the bands of muscular fibres about its centre. He has also shown that these liquids, very soon reach the kidneys, and pass off by urine; and was led to believe that the spleen was the channel of communication; an opinion, however, which his subsequent researches tended to disprove.*

* *Lectures on Comparative Anatomy*, p. 221.

The chyme passes from the stomach into the small intestines, where it soon changes considerably in appearance; it becomes blended with bile, and is separated into two portions, one of which is white as milk, and is termed *chyle*; the other passes on to the large intestines, and is ultimately voided as excrementitious. The chyle is absorbed by the *lacteals*, which terminate in the common trunk, called the *thoracic duct*; it is there mixed with variable proportions of lymph, and poured into the venous system.

The *excrements of animals* have been examined by Berzelius,* by Vauquelin,† and by Thaer and Einhoff. An abstract of these experiments has been published by Dr Thomson, in the 4th volume of his *System of Chemistry*.

2210. *Chyle* has been examined by several chemists, and their results are not widely different. During some physiological researches Messrs Brande and Brodie had an opportunity of collecting it in considerable quantities in several carnivorous and graminivorous animals, and an account of experiments upon it was presented to the Royal Society.‡

Chyle is an opaque white fluid, having a sweetish saline taste; its specific gravity is inferior to that of the blood. It exhibits slight traces of alkaline matter when tested by infusion of violets; soon after removal from the thoracic duct, it gelatinizes spontaneously, and afterwards gradually separates into a firm yellowish white coagulum, and a transparent colourless serum; so that, like the blood, it enjoys the property of spontaneous coagulation.

The *coagulum of chyle* possesses properties closely resembling those of the caseous portion of milk, and may hence be considered as a variety of albumen; the *serum of the chyle*, when heated, deposits a few flakes of albumen, and by evaporation to dryness affords a small proportion of a substance analogous to sugar of milk. Small portions of phosphate of lime, carbonate of soda, and common salt, may also be detected in the chyle. In these experiments Mr Brande found no distinctive difference in the chyle of graminivorous and carnivorous animals, he examined it from the horse, the ass, the dog, and the cat; Dr Marcet thinks that the former is less abundant in albumen than the latter.§||

2211. There can be little doubt that the bile performs an important part in the change which the chyme suffers in the small intestines. Whether the bile is absolutely necessary to the formation of chyle, is a question that has not been satisfac-

* Gehlen's *Journal*, vi.

† *Annales de Chimie*, xxix.

‡ Brande, in *Phil. Trans.* 1812, p. 91.

§ It is a curious question, whence the nitrogen, which constitutes an abundant ultimate principle of the chyle of herbivorous animals is derived; we find it in very small proportion only in their ordinary food, and yet I could discern no difference in the composition of the albuminous portion of their chyle, and that of animals fed exclusively on meat. (Brande.)

|| Thomson's *Annals*, vol. vii.

torily answered; but its importance is demonstrated by the emaciation that attends its deficiency, and by the disordered state of bowels that accompanies its imperfect secretion.*

2212. In chyle we cannot fail to observe a close approximation to blood; it is deficient only in colouring matter, and the albumen which it contains differs a little from that existing in the blood itself; it appears therefore, that the albumen is perfected, and the colouring matter formed, in the process of circulation; the saccharine principle of the chyle is also no longer perceptible.

Respiration.

2213. *Respiration* is the process of receiving a quantity of air into the lungs, whence, after having been retained a short time, it is again expelled in the action of expiration; and, if now examined, a portion of its oxygen is found converted into carbonic acid, and it is more or less loaded with aqueous vapour.

Number of respirations.

Obvious circumstances render it very difficult to ascertain the quantity of air taken into the lungs at each natural inspiration, as well as the number of respirations made in a given time; the former is perhaps about 15 or 16 cubic inches, and the latter about 20 in a minute.

Changes of the air respired.

The quantity of carbonic acid emitted at each expiration, varies at different periods of the day, and probably also in different individuals; it appears at its maximum during digestion, and at its minimum in the morning when the stomach is empty, and when no chyle is flowing into the blood. Dr Prout has shown that fermented liquors and vegetable diet diminish the proportion of carbonic acid, and that the same thing happens when the system is affected by mercury.†

Quantity of carbonic acid.

The air expired may be regarded, as containing, on an average, 3,5 per cent. of carbonic acid, though Messrs Allen and Pepys, in their valuable *Essay on Respiration*,‡ have estimated it at about twice that quantity; it amounted, in their experiments, to 27,5 cubic inches per minute, a quantity probably above the truth, when we reflect upon the comparative proportion of carbon existing in our food, and the other means of escape which it has from the body.§

From the experiments of Dr Edwards it would appear that the nitrogen of the air is not altogether passive during respiration, he found that during the respiration of the same animal, the quantity of nitrogen may one while be increased, at another time diminished, and at a third wholly unchanged. An augmentation of nitrogen was observable during summer. His experiments seem to leave no doubt that the blood, while circulating through the lungs, is capable of absorbing hydrogen, nitrogen, and oxygen gases and of emitting nitrogen. T.

* See Sir E. Home's *Lectures*, p. 468.

† Thomson's *System*, iv. 621.

‡ *Phil. Trans.* 1803.

§ The more recent experiments of Dr Edwards (*De l'Influence des agents Physiques sur la Vie*) have shown that the ratio between the gases varies with the animal.

The aqueous vapour contained in the expired air is secreted by the exhalents distributed over the surface of the air-vessels of the lungs; attempts have been made to estimate its quantity, but without success; it is probably liable to variation, and can scarcely be considered as a product of respiration.

2214. The change of colour in the blood is evidently owing to the action of the air, which takes place through the thin coats of the circulating vessels, and the end thus attained is the removal of the carbon from the venous blood, by which the colouring matter was obscured: the carbon to be thus readily soluble in oxygen must be in some peculiar state; a portion of it is also removed by the absorbents, and transferred to the glands situate at the root of the lungs between the subdivisions of the bronchiæ, which often contain a large portion of black matter.* The only chemical difference, then, which can be detected between arterial and venous blood, is the existence of a certain excess of carbon in the latter, which it gives off to oxygen, forming carbonic acid; the blood is thus fitted for the renovation of parts, for the formation of secretions, and for the sustenance of life by its action on the cerebral system; for although the heart does not directly refuse to circulate venous blood, paralysis and torpor ensue when blood, not aerated, passes into the vessels of the brain.

Change of colour in the blood.

2215. It has been shown that the blood suffers very important changes in the kidneys and liver; the function of *perspiration* also must be considered as connected with an alteration of the circulating fluid, for moisture, carbonic acid, and minute quantities of phosphoric acid, and saline matter, among which is common salt, are evacuated by the cutaneous vessels.

Perspiration.

2216. Different animals require very different quantities of oxygen for the purpose of respiration. Man, and warm-blooded animals, consume the largest quantity; the amphibious tribes not only require less, but can breathe in an atmosphere which will not support the life of the former; and many insects take such small quantity, as sometimes to have been supposed capable of living without air, which is not the case. In the production of carbonic acid all animals agree, and consequently the nature of the deterioration suffered by the air is similar throughout the animal creation.

Unequal quantity of oxygen necessary to different animals.

Fishes breathe the air which is dissolved in water; they therefore soon deprive it of its oxygen, the place of which is supplied by carbonic acid; this is in many instances decomposed by aquatic vegetables, which restore oxygen, and absorb the

* The conversion of venous into arterial blood appears not to be confined to the lungs. The disengagement of carbonic acid from the surface of the skin, and the corresponding disappearance of oxygen gas was demonstrated by Jurine and Abernethy; and although the accuracy of their results has been doubted by some persons it has been confirmed by others. However this may be in the human subject, the fact with respect to many of the lower animals is unquestionable. Dr Edwards has shown that this function compensates so fully for the want of respiration by the lungs, as to enable many of these animals in the winter season, to live for an almost unlimited period under the surface of water. T. 646.

carbon ; hence the advantage of cultivating growing vegetables in artificial fish-ponds. It has been ascertained by Biot, and verified by others, that the air-bladders of fish that live in very deep water are filled with a mixture of oxygen and nitrogen, in which the former greatly preponderates ; but in fish that are taken near the surface, the nitrogen is most abundant. In the *trygla lyra*, always caught in very deep water, the air-bladder contained 87 per cent. of oxygen : in the carp and roach, according to Fourcroy and Priestley, the air-bladder contains little else than nitrogen.*

Animal heat.

2217. The production of *animal heat* is perhaps the most recondite of all the functions ; the power appears to belong to all animals, though to some in a very inferior degree. The higher orders of animals always maintain a temperature of about 100° ; it varies a little in different parts of the body, the extremities and surface being a degree or two colder than the interior vital organs. This temperature is probably very little affected by external circumstances, a hot or cold atmosphere producing no corresponding change in the heat of the circulating blood.

Mr Brodie's experiments.

When the chemical changes that take place during respiration had been inquired into, and when it was found that the capacity of carbonic acid for heat was less than that of oxygen, it was supposed that the conversion of oxygen into carbonic acid was the cause of the rise of temperature : and as the heat of the lungs does not exceed that of the other parts, it was asserted that the air was absorbed by the blood, and that the production of carbonic acid, and consequent evolution of heat took place gradually during the circulation. To these opinions many strong objections have from time to time been urged by different physiologists, but their complete subversion followed the researches of Mr Brodie,† who found that the heart was capable of retaining its functions for some hours, and of carrying on circulation in a decapitated animal, and consequently independent of the influence of the brain, when respiration was artificially carried on. Under these circumstances it was observed, that although the change of blood from the venous to the arterial state was perfect, no heat was generated, and that the animal cooled regularly and gradually down to the atmospheric standard. In more than one instance Mr Brande examined, at his request, the expired air, and found that it contained as much carbonic acid as was produced by the healthy animal ; so that here circulation went on, there was the change of oxygen into carbonic acid, and the alteration of colour in the blood, and yet no heat whatever appeared to be generated.

In these cases a period was also put to the secretory functions ; and it has been observed by several other physiologists, that if the nerves that supply any of the glands are injured or

* Biot, *Memoire d' Arcueil*, i. and ii.

† *Phil. Trans.* 1812.

divided, there is a corresponding change or suspension of their secretion. Electricity has sometimes been supposed to have some connexion with the nervous influence, and the fact of some of the secretions being alkaline, while others are acid (corresponding to negative and positive influence), has been adduced in favour of the supposition, but experiment has gone little way to sanction such a notion, and although it has been proved that the nervous influence contributes to the generation of heat in animals, that it presides over the phænomena of secretion, as well as of voluntary motion, the actual cause of this influence, or energy, remains among those mysteries of nature which, doubtless, for the wisest purposes, are hidden to the human understanding.

ADDENDA.

Iodous Acid (361). The following method of preparing Iodous acid. this acid is preferable to that first published, as supplying it in a purer state, and in greater abundance. Chlorate of potassa is to be placed in a retort, with rather a large neck, and heated until the moisture is dissipated; then, at the time when oxygen is freely evolved from the salt, iodine is to be introduced by means of a metallic spoon as far as the body of the retort. The vapours of iodine which will be occasioned by the heat will immediately disappear, in consequence of their combination with the oxygen of the chlorate, and a strong effervescence will be perceived in the latter, occasioned by each portion of iodine with which it may combine; immediately yellow vapours will be perceived in the neck of the retort, and when they redden litmus paper, and a sufficient quantity of iodous acid has been obtained, the operation is to be finished, and the acid collected, the last portion being removed by a drop or two of water. All attempts to unite this acid with alkaline bases have failed, the iodine being precipitated.*

Oxide of Iodine was discovered in attempts to combine Oxide of iodine. iodine and oxygen directly together. It was obtained in the following manner. A copper tube about 20,6 inches in length, and 8 lines in diameter, having one extremity terminated in a screw, and the other by a small aperture about a line in diameter, was fixed upon two supports; the contracted extremity was curved, so as to permit of its introduction into the tubulure of a retort, without deranging its convenient inclination. A bladder filled with oxygen gas was attached to the screw. A long spirit-lamp with several wicks was placed beneath the lower part of the tube, so as, when necessary, to raise it to redness. Arrangements were also made for applying a lamp to the bottom

* According to M. Wöhler the iodous acid of M. Sementini is nothing more than a mixture of chloride of iodine and iodine. *Quart. Jour.* N. S. iii. 203.

of the retort, it having been found that to combine oxygen and iodine, both should be at a high heat.

The tube and retort being heated to redness, one person then presses the bladder to force heated oxygen into the retort, and another introduces a spoonful of iodine through the neck of the retort until it is brought under the jet of gas. The iodine is quickly converted into violet vapour, which fills the retort, but this soon disappears, and the retort neck becomes lined with a yellow transparent substance, almost solid; which, by the continuance of the operation, becomes more fluid, and flows forward as an oleaginous liquid. If the violet vapours are too abundant, the spoon is to be withdrawn for a little while, the introduction of oxygen being continued; when they have disappeared the iodine is to be re-advanced.

Properties.

The substance obtained in the commencement of this operation is oxide of iodine. It is of the consistency of a solid oil, has an acrid, disgusting taste, an odour similar to that of iodous acid, but weaker. It is slowly dissipated in the air, is very soluble in water and alcohol, producing amber-coloured solutions. If brought, in the solid state, into contact with a dry, combustible substance, it is decomposed, iodine being evolved. Phosphorus and potassium are inflamed by it. It changes the blue of litmus to green. If an alkali be poured into its solution, the latter is instantly rendered colourless; whereas if alkali be added to solution of iodous acid, iodine is precipitated.

If the addition of oxygen be continued after the formation of the oxide of iodine, then iodous acid is formed; and if the lamp applied to the bottom of the retort be at the same time removed to the neck, the formation of the iodous acid will be much facilitated.

Finally, oxide of iodine is always formed when iodine is heated in close vessels containing air, and air may be used in place of oxygen in the process above described. If iodine be put into a retort, and then a second be sealed hermetically to the first, a small capillary hole being left in the neck; the iodine being heated successively, first in one part and then in another of the apparatus, whenever it assumes the solid form, will gradually change into oxide of iodine.*

Iodo fluoric acid.

Iodo-fluoric Acid.—On mixing vapours of iodine and fluoric acid in a glass globe, the latter became lined with a white film, and the iodine was absorbed; when the action appeared to have ceased, water was poured into the globe and caused an immediate deposition of gelatinous silica. By filtration a liquid was obtained, yellow, from free iodine, but becoming colourless by heat; carbonate of ammonia was then added in excess, which separated the rest of the silica, and carbonic acid gas was disengaged. The filtered solution was very alkaline, but by ebullition gradually became quite acid. Being afterwards cooled it deposited many small crystals of a fine golden yellow colour,

* *Giornale de Fisica*, ix. p. 337.

† M. Varinsky, in *Bull. Univ. A.* viii. 360.

and possessing all the properties of a strong acid. They dissolved more readily in hot than in cold water, and with caustic potassa, produced a gelatinous salt, having a very disagreeable bitter taste. These crystals are iodo-fluoric acid.†

Fluo-silicic Acid.—To prepare the fluo-silicic acid in sufficient quantity, M. Maus uses a very large retort with a long neck: he puts into it the mixture of fluor-spar and glass, and adds sulphuric acid, to about three times the amount of the fluor-spar in weight, and mixes the whole well. A large globe with a long neck is then provided, and a sufficient quantity of water put into it; the neck of the retort is introduced; the globe shaken, to moisten the interior with water, and the fluo-silicic gas evolved by the application of heat. When it arrives in the globe it condenses in the water, and as soon as the quantity of silica produced retards the contact of the gas and water, the globe is again shaken and the operation continued. In this way no gas escapes, and the water soon becomes saturated with the acid; the silica is easily separated.*

Fluo-silicic acid.

Liquid Ammonia (528).—The following process for the preparation of liquid ammonia is said to produce double the quantity obtained by the usual methods. A tubulated retort is to be put into a sand-bath, and connected with a small balloon placed on a small furnace; a tube is to proceed from the balloon to a flask which is to be supplied with a safety tube, and with another tube dipping into a mercurial bath. Equal parts of sal-ammoniac and hydrated lime are to be used; the lime is to be made into a cream with water, and put into the retort, and then the powdered sal-ammoniac added; after being well mixed the retort is to be closed; water, equal in weight to the sal-ammoniac, is to be put into the flask; the retort in the sand-bath to be heated, and the balloon moderately warmed. As the ammoniacal gas is disengaged it will be absorbed by the water in the flask. By managing the fire properly, and distilling the portion of impure ammonia in the balloon, pure ammonia of the sp. gr. of .910 will be obtained, 16 lbs being produced for every 10 lbs of sal-ammoniac employed.†

Preparation of liquid ammonia.

Habitudes of Sulphuric Acid.—M. Bellani found that the glacial sulphuric acid of Nordhausen, like common concentrated sulphuric acid, had a specific gravity of 1,843 at 50° F. and that it congealed at 53°,6. When it was exposed to air, at nearly a freezing temperature, the surface absorbed water and became covered with crystals, which when separated and fused, gave a liquid of sp. gr. 1,78. On the other hand, when glacial acid was mixed with enough water to give a fluid of sp. gr. 1,793, it, when frozen, supplied crystals which, being melted, gave a liquid of sp. gr. 1,78, whilst the residual liquid had a sp. gr. of 1,73.

Habitudes of sulphuric acid.

When sulphuric acid, concentrated or diluted, congeals, it undergoes a diminution of volume, almost equal in extent to

* *Ann. de Phys.* 1827, 83.

† M. Bizio in *Bull. Univ.* C. xii. 88.

the increase which takes place with water under similar circumstances. Thus 1000 parts of fluid glacial acid become 925 parts by volume of solid acid; and 1000 parts of acid of sp. gr. 1.78, by congealing, become 910 parts, from which it would appear that the water in the diluted acid does not undergo the same change in solidifying, as when in the free state.*

Oxide of carbon.

Oxide of Carbon.—M. Dumas has proposed the following method of preparing this gas: he mixes salt of sorrel with five or six times its weight of concentrated sulphuric acid; the mixture when heated in a proper apparatus, yielded a considerable quantity of a gas composed of equal parts of carbonic acid gas and oxide of carbon; after absorbing the carbonic acid gas by potassa, the oxide of carbon remains in a state of purity. This process may be employed for examining the salt of sorrel of commerce. Bitartrate of potassa treated in the same manner gives oxide of carbon, carbonic and sulphurous acids, and the liquor becomes black by the deposition of carbon. The salt of sorrel on the contrary, never yields sulphurous acid, and the sulphuric acid employed remains perfectly limpid and colourless.†

Aluminum.

Aluminum (1200).—M. Wöhler has given the following account of the preparation and properties of aluminum. The method of preparing it is founded on the inoxidability of this metal by water. When an attempt was made to heat chloride of aluminum with potassium in a tube, the action was so strong and the extrication of heat so considerable, that the apparatus was instantly broken. A small platinum crucible was therefore employed, the cover of which was kept on by a wire of the same metal. At the moment of reduction the crucible became intensely red-hot, both within and without, although it was but slightly heated: the metal of the crucible was not sensibly acted upon. The operation may also be effected in a porcelain crucible with a cover attached. Some small pieces of potassium of about the size of a pea, and not more than ten at once, are placed in the crucible, and upon them are put an equal number of pieces of aluminum of the same size; the crucible is to be heated with the spirit-lamp, at first gently, and afterwards more strongly, and until the spontaneous incandescence of the matter ceases. Excess of potassium is to be avoided; for after it was oxidized, it would dissolve a portion of the aluminum. The reduced mass is generally completely fused, and is of a blackish grey colour. When all is cold, the crucible is to be thrown into a large vessel of water; a grey powder is soon deposited, which, when looked at in the sunshine, appears to be entirely composed of small metallic plates; the powder is to be washed with cold water and then dried: it is the metal of alumina.

Properties.

Aluminum somewhat resembles platinum in powder. M. Wöhler discovered some scaly coherent particles, which had

* *Giornale di Fisica—Bull. Univ. A. viii. 316.*

† *Ann. de Chim.*

the colour and splendour of tin. Under the burnisher it readily assumes the appearance of this metal; rubbed in an agate mortar, it seems to be a little compressible, and unites into larger scales, with a metallic lustre; and it leaves in the mortar traces of a metallic appearance. When heated in the air, until it is ignited, it inflames and burns with great rapidity; the product is the white oxide of aluminum in a hard mass. Reduced to powder and blown upon in the flame of a candle, each particle suddenly becomes an inflamed point, the splendour of which is not less than that of the sparks of iron burning in oxygen gas. In pure oxygen gas aluminum burns with so dazzling a light, that the eyes can scarcely bear it; the heat generated is so considerable that the oxide produced is partly fused. The particles which have been fused are yellowish, and as hard as corundum; they do not merely scratch, but they cut glass. In order that aluminum may burn in oxygen gas it must be heated to redness.

Aluminum is not oxidized by water, and this fluid may spontaneously evaporate from the metal without its being in the least tarnished; when, however, the water is nearly at its boiling point, the metal is slowly oxidized, and hydrogen is liberated.

Sulphuric and nitric acids when cold do not act upon aluminum; when heated, concentrated sulphuric acid readily dissolves it, and without the evolution of sulphurous acid.

Action of
acids,

Aluminum introduced into a solution of caustic potassa, even when weak, dissolves readily, and with the evolution of hydrogen; the solution is perfectly clear; the same solution takes place in ammonia; and it is surprising to observe how much of this earth the ammonia is capable of uniting with: the evolution of hydrogen is similar to that with potassa. When aluminum is heated to dull redness, and exposed to a current of chlorine, it inflames and is converted into chloride, which sublimates as fast as it is formed.

— of potassa.

Chloride of Aluminum.—M. Wöhler obtains chloride of aluminum, for the purpose of procuring the metal from it, by the following process: alumina precipitated by excess of carbonate of potassa, was well washed and dried, and then made into a thick paste with powdered charcoal, sugar and oil; this paste was then heated in a covered crucible until all the organic matter was destroyed. By these means any substance is mixed very intimately with carbon: the product while it was hot, was put into and made to fill a porcelain tube, which was placed in a furnace of an oblong form. One end of the tube was connected with another tube containing fused chloride of calcium, and this with an apparatus for the evolution of chlorine: the other end of the tube opened into a small tubulated receiver, provided with a conducting tube. When the apparatus was full of chlorine, the tube and its contents were made red hot. The chloride of aluminum was readily formed; a small portion was carried over with oxide of carbon, which fumed strongly on coming into contact with the air. The chlorine was long

Chloride of
alumina.

retained by the mass of matter. The receiver contained chloride of aluminum in the state of powder. After an hour and a half the chloride obstructed the end of the tube (though an inch in diameter) which passed into the receiver; this caused the stoppage of the process.

On taking the apparatus to pieces, it was found that all that part of the tube which passed through the furnace was filled with chloride of aluminum, and it weighed more than an ounce. It consisted partly of an aggregation of long crystals, and partly of a firm mass, which was readily detached from the tube and was of a pale yellowish green colour, semitransparent, and of a lamellated and distinctly crystalline texture. When brought into contact with the air, it fumed feebly, gave a smell of muriatic acid, and soon became a transparent fluid. When thrown into water, it dissolved with strong hissing, accompanied with so much heat, that the fluid, when the quantity is small, boils rapidly: according to M. Oersted, the temperature is not much higher than that of boiling water. Its fusing and vaporizing points seem to be the same. Chloride of aluminum may be preserved without any alteration in naphtha; when heated with this oil it liquefies, and sinks to the bottom of the vessel, in the form of a reddish-brown liquid, upon which potassium exerts no action.

Sulphuret of
aluminum.

Sulphuret of Aluminum.—When sulphur is suffered to drop upon aluminum in a state of vivid ignition, the mixture becomes strongly incandescent, and a black frit is formed; it is semi-metallic in appearance, and when polished is of a shining iron black colour. Exposed to the air it emits the smell of sulphuretted hydrogen, swells, and falls into a greyish-white powder; when applied to the tongue, it occasions a hot penetrating sensation; when thrown into water it is converted into a grey powder of alumina, accompanied with a rapid disengagement of sulphuretted hydrogen. Sulphate of alumina when heated to redness in contact with hydrogen, loses its acid, but the earth is not reduced.

Sulphuretted Hydrogen and Aluminum.—When chloride of aluminum is sublimed in a small retort, and a strong current of sulphuretted hydrogen is at the same time made to enter its neck, it is absorbed; and a very white sublimate is formed, partly in the state of pearly, transparent, scaly crystals, and partly in that of a brittle mass. In contact with the air the sublimed matter moistens rapidly, sulphuretted hydrogen is disengaged, and chloride of aluminum remains in solution. When sublimed in a tube, it evaporates with the evolution of sulphuretted hydrogen equal to from 30 to 40 times its volume, which, however, cannot be the whole of the gas, because the combination is formed at a high temperature. When put into water the sublimate is decomposed with the same violence as the pure chloride; much sulphuretted hydrogen is disengaged, and the solution is rendered turbid by the precipitation of sulphur.

Phosphuret of Aluminum.—Aluminum heated to redness in the vapour of phosphorus, combines with it with vivid inflammation; the product is a blackish grey pulverulent substance, which, under the burnisher, assumes a deep grey metallic lustre, and exhales a smell of phosphuretted hydrogen; when thrown into water, it occasions the evolution of phosphuretted hydrogen, which is not spontaneously inflammable. Phosphuret of aluminum.

Seleniuret of Aluminum.—Selenium when mixed with the metal of alumina, and heated to redness, combines with it, producing strong inflammation. The seleniuret thus obtained is a black powder, which being rubbed becomes of a dull metallic aspect. When exposed to the air it continually exhales a smell of seleniuretted hydrogen; in water the disengagement of this gas is very rapid, and the water is quickly reddened by a portion of precipitated selenium. Seleniuret,

Arseniuret of Aluminum.—Arsenic in powder heated to redness with aluminum, combines with it. The compound is a powder of a deep grey colour, which by rubbing acquires a dull metallic appearance, and when exposed to the air it exhales a faint smell of arseniuretted hydrogen; when cold, the disengagement is slow, but is much accelerated by heat. Arseniuret,

Telluret of Aluminum.—When the powder of tellurium was put into a tube with aluminum, much heat was excited, and the mixture was thrown with explosion out of the tube; this inconvenience is avoided by not powdering the tellurium. The product is a metalline, brittle, black frit, which when exposed to the air emits an intolerable odour of telluretted hydrogen; and when thrown into water it evolves the same gas with rapidity.* Telluret.

Chromic Acid (1537).—M. Maus prepares chromic acid by the following process. A hot and concentrated solution of the bichromate of potassa is to be decomposed by fluo-silicic acid, the liquid is to be filtered and evaporated to dryness; the acid thus dried is to be dissolved in as small a quantity of water as possible, and the clear fluid *decanted* from the deposit of fluo-silicate of potassa which has passed the filter. The separation of this portion must not be made by a filter, for in this state the chromic acid attacks the paper, and is itself converted into oxide of chrome. Chromic acid.

Gaseous Fluoride of Manganese.—Ordinary chameleon mineral (1222) was mingled with half its weight of powdered fluor-spar, and acted upon by sulphuric acid, an instant disengagement of purple red vapours in large quantity took place. The same experiment was made in a platinum retort, and the gas conducted into a platinum crucible containing a little water; it was absorbed, and the water acquired the purple colour of manganese, and was acid in its properties. On opening the retort before the action was over, it was found filled with a *yellow* Gaseous fluoride of manganese.

* Hensman's *Rep. de Chim.* Jan. 1828; and *Ann. Philos. N. S.* xx. 147.

gas, instantly turning purple by contact with the air. To prove that the yellow gas did not arise from nitre, a pure crystallized manganate of potassa was made by heating to dull redness equal parts of hydrated potassa and peroxide of manganese. This, mixed with its weight of powdered fluor-spar, free from silica, was acted on by sulphuric acid as before, the gas passed first into a glass receiver and from thence into water. For the first moment the receiver was filled with a greenish yellow gas, but this soon disappeared from action upon the glass; the latter was strongly corroded and covered with a brown substance, which gave an intense purple colour to water. The water into which the gas passed soon became red, and was covered with a crust of rose-coloured silica. On dismantling the apparatus, the glass receiver was found filled with fluo-silicic gas, and the retort, as before, with a yellow gas, becoming purple instantly in the air. Hence it appears that a gaseous fluoride of manganese was formed, of a greenish yellow colour, which, with air, formed a red purple cloud, dissolved in water, producing a red purple colour, and was decomposed by glass into manganic acid and fluo-silicic gas.

The red solution of the gas in water rapidly dissolved copper, mercury, and silver, without the evolution of gas; fluoride of silver, &c. and a proto-fluoride of manganese being formed. The purple red solution when evaporated slowly in a platinum vessel, continually develops oxygen and vapours of fluoric acid; and there remains a brilliant brown substance, which, by water, is converted into a black subfluoride of manganese.*

Silicate of Soda—See Mr Walcker's experiments in *Quart. Jour.* vi. N. S. 371.

Separation of Lime from Magnesia—See Mr Walcker's experiments in *Quart. Jour.* vi. N. S. 374.

* M. Wöhler in *Ann. de Chim.* xxxvii. 101.

APPENDIX.

Dr Wollaston's Synoptic Scale of Chemical Equivalents.—

The paper, by its author, describing the nature of the scale and the manner of ascertaining the numbers appropriated to the different substances upon it, is inserted in the Philosophical Transactions for 1814. The scale itself, as purchased of the instrument-maker, consists of a moveable slider with a series of numbers upon it, from 10 to 320, on each side of which and on the fixed part of the scale, are set down the names of various chemical substances.

The scale is founded on three important points,—the constancy of composition in chemical compounds (77); the equivalent power of the quantities that enter into combination (79, &c.); and the properties of a logometric scale of numbers.

It will be found that the numbers are so arranged, that at equal intervals they bear the same proportion to each other. The student will easily observe and understand this, by measuring a few distances upon the scale with a pair of compasses, or even a piece of paper. If his paper extend from 10 to 20, it will also extend from 20 to 40, or from 55 to 110, or from 160 to 320. Whatever number is at the upper edge of the paper will be doubled at the lower. If any other distance be taken, the same effect will be observed. If, for instance, the paper extends from 10 to 14, then any other two numbers found at its upper and lower edge will be in the same proportion as these two numbers 10 and 14. Thus make the upper number 100, and the lower number will be 140.

Now supposing that the paper were cut of such a width that, one of its edges being applied upon the scale to the number representing the equivalent of one body, the other should coincide with the number of the equivalent of a second body; then upon moving the paper, wherever it was placed over the numbers, those at its upper and lower edges would still represent the corresponding proportional quantities of the two bodies as accurately as at first, because the numbers at equal distances on the scale are proportional to each other. Thus suppose the upper edge were made to coincide with 40 and the lower with 78, then the upper edge might be called sulphuric acid, and the lower baryta; and this width once ascertained, the paper wherever applied upon the scale, would shew at its lower edge the quantity of baryta necessary to combine with the quantity of sulphuric acid indicated by its upper edge.

It is evidently of no consequence whether the paper be moved up and down over the scale, or the line of numbers be moved higher and lower, to bring its different parts to the edges of the

paper. And supposing the piece of paper just described to be pasted upon the side of the scale, then by moving the latter any of the numbers might be made to coincide with the upper or lower edge at pleasure, and consequently the quantity of sulphuric acid necessary to combine with any quantity of baryta, and vice versa, ascertained by mere adjustment and inspection of the scale. Or if, instead of referring to the separate piece of paper, marks were to be made on the side of the scale at 40 and 78, and named sulphuric acid and baryta, the same object would be attained, and the same method of inquiry rendered available.

Other substances are to be put down upon the scale exactly in the same manner. Thus the scale being adjusted until the number 40 coincides with the sulphuric acid already marked, then sulphate of baryta is to be written at 118, and thus its place is ascertained; nitrate of baryta at 132; soda at 32; sulphate of soda at 72; and a similar process is to be adopted with every substance, the number of which has been ascertained by experiment. The instrument, which in this state merely represents the actual numbers supplied by experiment, will faithfully preserve the proportions thus set down, whatever the variation of the position of the slider may be. It is therefore competent to change all the numerical expressions to any degree required, the knowledge of one only being sufficient first by adjustment, and then by inspection to lead to the rest.

A few illustrations of the powers and uses of this scale will be sufficient to make the student perfect master of its nature and applications. Suppose that in analysing a mineral water, the sulphates in a pint of it have been decomposed by the addition of muriate of baryta, and the resulting sulphate of baryta washed, dried, and weighed: from its quantity may be deduced the exact quantity of sulphuric acid previously existing in the mineral water. Thus, if the sulphate of baryta amount to 43,4 grains, the slider is to be moved until that number is opposite to *sulphate of baryta*, and then at *sulphuric acid* will be found the quantity required, namely 14,7 grains. In the same manner the scale will give information of the quantity of any substance contained in a given weight of any of its compounds; these having previously been deduced from experiment, and accurately set down on the table in the manner just explained.

If it be desired to know how much of one substance must be used in an experiment to act upon another, it is evident that the equivalent must be taken, and this may be learned from the scale. Suppose that a pound of sulphate of baryta has been mixed with charcoal, and well heated, to convert it into a sulphuret, and that by the addition of nitric acid it is to be converted into nitrate of baryta. The quantity of acid which will probably be required may be learned by bringing 100 to sulphate of baryta, and then by looking for the number opposite nitric acid: it will be found to be 46. But this represents the

quantity of dry acid; casting the eye therefore lower down, upon liquid nitric acid of a specific gravity of 1,50, it will be found that 61 lbs or a little more, is the equivalent for 100 lbs and consequently that 61 hundredth parts, or somewhat above six-tenths of a pound of such acid, will be sufficient for the pound of sulphate of baryta operated with.

If a certain weight of carbonate of baryta be required in that moist and finely divided state, in which it is obtained by precipitation, and in which it cannot be weighed, the accuracy of the quantity may be insured by taking the equivalent of dry muriate, or nitrate of baryta, precipitating it by an excess of carbonate of potassa, and then washing off the salts which remain in solution. Suppose 100 grains of the carbonate were required; by bringing that number to carbonate of baryta, it will be found that the quantity of dry muriate necessary will be 105,8 parts, and the quantity of nitrate 133,4; and if the quantity of carbonate of potassa necessary for this purpose be also required, it will be found opposite the name of that substance on the scale, to be a little less than 70 parts, so that 5 or 10 parts more will ensure a satisfactory excess.

The second paragraph of Dr Wollaston's description of this scale may be transcribed, as a further illustration of the powers of the instrument. "If, for instance, the salt under examination be the common blue vitriol, or crystallized sulphate of copper, the first obvious questions are—(1) How much sulphuric acid does it contain? (2) How much oxide of copper? (3) How much water? He [the analytic chemist] may not be satisfied with these first steps in the analysis, but may desire to know further the quantities (4) of sulphur, (5) of copper, (6) of oxygen, (7) of hydrogen. As means of gaining this information, he naturally considers the quantity of various re-agents that may be employed for discovering the quantity of sulphuric acid (8), how much baryta, (9) carbonate of baryta, or (10) nitrate of barytes, would be requisite for this purpose? (11) How much lead is to be used in the form of (12) nitrate of lead; and when the precipitate of (13) sulphate of baryta, or (14) sulphate of lead are obtained, it will be necessary that he should also know the proportion which either of them contains of dry sulphuric acid. He may also endeavour to ascertain the same point by means of (15) the quantity of pure potassa, or (16) of carbonate of potassa requisite for the precipitation of the copper. He might also use (17) zinc, or (18) iron, for the same purpose, and he may wish to know the quantities of (19) sulphate of zinc, or (20) sulphate of iron, that will then remain in the solution."

All these questions and points are answered by moving the slider until the number expressing the quantity operated with coincides with *sulphate of copper crystallized*. 5, *Water*. Let it for instance be 100: this being brought opposite crystallized sulphate of copper, the information relative to all the above points, except the sixth and seventh, is supplied by mere

inspection. The sixth may be supplied by subtracting (5) the quantity of copper from (2) the quantity of oxide of copper, or by halving the quantity at 2 oxygen, or taking the third of that at 3 oxygen. The seventh relates to the quantity of hydrogen in the 5 water present in the salt; this quantity of hydrogen does not come within the line of numbers, but may easily be obtained by doubling the quantity of water, or doubling the quantity of the salt used, which will then bring 10 hydrogen into the scale, and the half of this is to be taken as the quantity in 5 water, or in 100 grains of the salt. Putting therefore 200 to sulphate of copper, 10 hydrogen, is indicated as 17 parts nearly, when of course the half of this, or 8,5 parts, is the quantity in 100 grains of the crystallized salt of copper.

Whenever it thus happens that the number known or the number sought for is out of the scale, then some convenient multiplier of the numbers may be used. The most convenient method is to use the tens or the hundreds as units, or what is the same thing, to consider for the time that decimal points are inserted between the units and the tens, or between the tens and the hundreds of all the numbers on the scale. Thus if it were required to ascertain how much magnesia and sulphuric acid were contained in a pound of crystallized sulphate of magnesia, no 1 exists upon the scale, and of course no fractions or small parts of 1; but imagine decimal points between the tens and the hundreds, then 10 upon the scale becomes one-tenth, 22 twenty-two hundredths, 100 one, 220 two and two-tenths and so on. Bringing therefore 100 to crystallized sulphate of magnesia, it represents the 1 pound, and by inspection it will be found that it contains 16 hundredths of a pound of magnesia, and $32\frac{1}{2}$ hundredths of a pound of sulphuric acid.

As another illustration; suppose that the quantity of magnesia in 50 lbs of crystallized Epsom salt were required; upon bringing 50 opposite the name of the salt, the quantity of magnesia will be found smaller than any quantity expressed upon the scale: but all that is necessary to obtain the answer is, to double the quantity of the salt, and then to halve the quantity of magnesia indicated; in which way it will be found that the 50 lbs contain about 8 lbs of the earth.

These *Synoptic scales* are generally constructed of paper or wood. Those on paper are first laid down accurately upon copper, are then engraved, impressions worked off upon paper, and these impressions pasted upon a wooden frame and slider prepared for them. It is almost impossible that these scales should be accurate, because of the extension and contraction of paper when it is damped, and again dried, and the facility with which it yields to mechanical impressions, and may be stretched when in a moistened state. When the paper is pasted to make it adhere to the wood, it extends considerably in all directions; and though this extension, as caused merely by dampness, would not very much surpass that which had taken place in the paper

when damped previous to its receiving the ink from the copper-plate, it is seriously increased by the rubbing and other mechanical action employed, both in applying the paste from a brush, and in afterwards bringing the paper into close contact at every part with the wood. These scales should never therefore be considered as accurate when they first come from the instrument-maker. They may be examined by a pair of compasses or a piece of paper, as before described (p. 589), to ascertain how nearly, equal intervals on the scale of numbers, accord with equal proportions between the numbers at the extremities of those intervals, and thus the degree of error in them, and the part where it exists to the greatest extent may be observed: but it will be useless to do so with the view of finding one so accurate as to dispense with calculation in exact analytical experiments.

Those scales, which are laid down directly upon wood, though not liable to the same sources of error as the paper scales, are still seldom, if ever, so accurate as to compete with calculation.

The errors just referred to, relate to the accuracy of the scale of numbers, and its proportional value in every part. Others relate to the imperfect and inaccurate results of the experiments, by which the numbers representing the equivalent or combining quantities of bodies are obtained. If an inaccurate result be mistaken for a correct one, and the proportional number of a body be entered erroneously upon the scale, it is evident that all estimations of substances including that body, which are given by the scale, must involve this original inaccuracy. Whenever therefore a more accurate determination of the number of a body is obtained than was before possessed, its place on the scale should be corrected; and as the equivalent numbers of substances, previously undetermined, are satisfactorily ascertained, the substances themselves should be put upon the scale in their proper situations, as before described.

In consequence of the unavoidable errors in the scale of numbers, which, however small, still interfere in the investigation of complicated cases, and the determination of accurate conclusions, the instrument should only be used in those instances where accuracy within a certain degree is sufficient for the purpose. All nicer results should be obtained by calculation from a *table* of equivalents: if, for instance, the quantity of sulphuric acid in 64,7 grains of sulphate of baryta were required to two or three places of decimals, it would be better to take the equivalent numbers of sulphate of baryta and sulphuric acid from such a table, and to say, as the first number is to the second, so is 64,7 to the quantity of sulphuric acid it contains, than to work with the scale. The present determination of the sulphate of baryta is 118, and that of sulphuric acid 40, hydrogen being 1 or unity, and as 118 is to 40, so is 64,7 to 21,932 very nearly. It will be impossible to ascertain this last number

accurately on an ordinary scale, or to observe how far it differs from 22.

There are numerous tables of equivalents published in different chemical works. Whichever may be adopted should be examined from time to time, and the numbers affixed to bodies on it corrected, whenever they are more accurately determined.

It has been shewn by Gay-Lussac and others, that all gases and all volatile substances when in the state of vapour, combine or act chemically in volumes, which have very simple relations to each other. Thus a volume of hydrogen combines with half a volume of oxygen to form a quantity of water, which, if raised into vapour, and corrected for temperature, &c. is equal in bulk to the volume of hydrogen used. A volume of hydrogen combines with a volume of chlorine, to form two volumes of muriatic acid; and with a volume of the vapour of iodine to form two volumes of hydriodic acid. Three volumes of hydrogen combine with one volume of nitrogen to form two volumes of ammonia; and half a volume of oxygen on combining with carbon to form carbonic oxide, becomes a whole volume.

Relations of this simple kind have been found to exist in the case of every volatile body, which has been particularly examined in reference to this point. These volumes once ascertained, may be considered in the relation of equivalents, and their proportions are so simple, as to be remembered without the least difficulty: it is therefore highly advantageous in all tables of chemical equivalents, to place small diagrams by the sides of the substances and their numbers, which may represent the volumes of the equivalents when brought into the state of gas or vapour. For it requires no great power of discernment to perceive that, if bodies combine in definite weights, and also in simple ratios of volumes, these volumes so combining must contain the weights previously found to be definite: for whether two substances which combine to form a third, are observed by weight or volume, still they combine only in one proportion.

So arranged, the table will have an appearance of the following kind:

| | | | | |
|----------------|-----------|-----|-----------|--------------------------|
| Hydrogen | | 1 | | <input type="checkbox"/> |
| Oxygen | | 8 | | <input type="checkbox"/> |
| Chlorine | | 36 | | <input type="checkbox"/> |
| Iodine | | 125 | | <input type="checkbox"/> |
| Water | | 9 | | <input type="checkbox"/> |
| Muriatic acid | | 37 | | <input type="checkbox"/> |
| Hydriodic acid | | 126 | | <input type="checkbox"/> |
| Ammonia | | 17 | | <input type="checkbox"/> |

and will be found very useful when referred to for gaseous or vaporous substances. The proportions of these volumes are

much more easily remembered than the proportions of their equivalent numbers; which, added to the facility with which the bulk of gases or vapours are ascertained, may often properly induce the chemist to dispense with the determination of weights, and work with volumes only.*

Conducting power for Heat of the Principal Metals and some Earthy Substances.—The following results have been obtained by M. Despretz, the experiments having been made with extreme care.

| | | | | | | | | |
|------------|---|---|---|---|---|---|---|--------|
| Gold | - | - | - | - | - | - | - | 1000,0 |
| Silver | - | - | - | - | - | - | - | 973,0 |
| Platinum | - | - | - | - | - | - | - | 981,0 |
| Copper | - | - | - | - | - | - | - | 898,2 |
| Iron | - | - | - | - | - | - | - | 374,3 |
| Zinc | - | - | - | - | - | - | - | 363,0 |
| Tin | - | - | - | - | - | - | - | 303,9 |
| Lead | - | - | - | - | - | - | - | 179,6 |
| Marble | - | - | - | - | - | - | - | 23,6 |
| Porcelain | - | - | - | - | - | - | - | 12,2 |
| Fire-brick | - | - | - | - | - | - | - | 11,4 |

That platinum should be above copper, and even silver, induces us to insert the description of the experiment. All the bars used were square prisms. Cavities were made in them at equal distances of 10 centimetres, to receive the bulbs of small thermometers. The side of the section, except for the two last bodies in the list, was equal to 21 millimetres. The bars were covered with the same varnish, to give them an equal radiating power. The bar experimented with, was heated at one extremity by a small stove, which has the advantage of being governed readily, and of causing but little heat in the place. The temperature of the air was ascertained by a sensible thermometer, and it was found easy to make it nearly uniform for the whole of an experiment. Each experiment continued six hours, and it was only after two or three hours, that all the thermometers became stationary. The thermometer nearest to the source of heat soon acquires the temperature at which it is to be retained stationary, and then the heat is managed so that it shall not rise or fall by that instrument, until the experiment is finished.

The following is the form of an experiment.

| Bar of Copper. | | Temperature of the Air 17°,03 C. | |
|----------------|--------------|----------------------------------|---|
| Thermometer. | Temperature. | Excess above the tem. of air. | Quotient of the sum of two excesses divided by the intermediate excess. |
| 1st | 83,44 | 66,36 | |
| 2d | 63,36 | 46,28 | 2,14 |
| 3d | 49,70 | 32,62 | 2,15 |
| 4th | 41,40 | 24,32 | 2,11 |
| 5th | 35,71 | 18,63 | 2,17 |
| 6th | 33,26 | 16,18 | |

It is admitted as having been demonstrated that the conductivity is proportional to $\left(\frac{1}{\log x}\right)$; x being obtained by the equation $x + \frac{1}{x} = q$; in which q is the coefficient of the sum of the excess, by the intermediate excess; and according to the results obtained with good conductors, as gold, silver, platinum, copper, iron and zinc, these satisfy the experimental series which is indicated by calculation. The same is not the case with bad conductors.

Wood conducts so feebly, that a bar 21 millimetres does not become sensibly heated a few centimetres from one of its extremities so far raised in temperature as to carbonize the substances.—*Annales de Chimie*, xxxvi. 422.

* From Faraday's *Chemical Manipulation*.

- 1.—Table, consisting of *Frigorific Mixtures*, having the Power of generating, or creating, Cold, without the aid of Ice, sufficient for all useful and philosophical purposes, in any part of the World at any Season.

Frigorific Mixtures without Ice.

| MIXTURES. | Thermometer sinks. | Deg. of cold produced. |
|---|-------------------------------------|------------------------|
| Muriate of ammonia . . . 5 parts Nitrate of potassa . . . 5 Water 16 | From $+50^{\circ}$ to $+10^{\circ}$ | 40 |
| Muriate of ammonia . . . 5 parts Nitrate of potassa . . . 5 Sulphate of soda . . . 8 Water 16 | From $+50^{\circ}$ to $+4^{\circ}$ | 46 |
| Nitrate of ammonia . . . 1 part Water 1 | From $+50^{\circ}$ to $+4^{\circ}$ | 46 |
| Nitrate of ammonia . . . 1 part Carbonate of soda . . . 1 Water 1 | From $+50^{\circ}$ to -7° | 57 |
| Sulphate of soda . . . 3 parts Diluted nitric acid . . . 2 | From $+50^{\circ}$ to -3° | 53 |
| Sulphate of soda . . . 6 parts Muriate of ammonia . . . 4 Nitrate of potassa . . . 2 Diluted nitric acid . . . 4 | From $+50^{\circ}$ to -10° | 60 |
| Sulphate of soda . . . 6 parts Nitrate of ammonia . . . 5 Diluted nitric acid . . . 4 | From $+50^{\circ}$ to -14° | 64 |
| Phosphate of soda . . . 9 parts Diluted nitric acid . . . 4 | From $+50^{\circ}$ to -12° | 62 |
| Phosphate of soda . . . 9 parts Nitrate of ammonia . . . 6 Diluted nitric acid . . . 4 | From $+50^{\circ}$ to -21° | 71 |
| Sulphate of soda . . . 8 parts Muriatic acid 5 | From $+50^{\circ}$ to 0° | 50 |
| Sulphate of soda . . . 5 parts Diluted sulphuric acid . . 4 | From $+50^{\circ}$ to $+3^{\circ}$ | 47 |

N. B.—If the materials are mixed at a warmer temperature, than that expressed in the Table, the effect will be proportionably greater; thus, if the most powerful of these mixtures be made, when the air is $+85^{\circ}$, it will sink the thermometer to $+2^{\circ}$.

2.—Table, consisting of *Frigorific Mixtures*, composed of *Ice*, with *Chemical Salts and Acids*.

Frigorific Mixtures with Ice.

| MIXTURES. | Thermometer sinks. | Deg. of cold produced. |
|---|--|------------------------|
| Snow, or pounded ice . . 2 parts Muriate of soda . . . 1 | From any temperature <div> to — 5° to — 12° to — 18° to — 25° </div> | * |
| Snow, or pounded ice . . 5 parts Muriate of soda . . . 2 Muriate of ammonia . . 1 | | * |
| Snow, or pounded ice . . 24 parts Muriate of soda . . . 10 Muriate of ammonia . . 5 Nitrate of potassa . . 5 | | * |
| Snow, or pounded ice . . 12 parts Muriate of soda . . . 5 Nitrate of ammonia . . 5 | | * |
| Snow 3 parts Diluted sulphuric acid . . 2 | From + 32° to — 23° | 55 |
| Snow 8 parts Muriatic acid 5 | From + 32° to — 27° | 59 |
| Snow 7 parts Diluted nitric acid . . . 4 | From + 32° to — 30° | 62 |
| Snow 4 parts Muriate of lime 5 | From + 32° to — 40° | 72 |
| Snow 2 parts Cryat. muriate of lime . . 3 | From + 32° to — 50° | 82 |
| Snow 3 parts Potassa 4 | From + 32° to — 51° | 83 |

N. B.—The reason for the omissions in the last column of this Table, is, the thermometer sinking in these mixtures to the degree mentioned in the preceding column, and never lower, whatever may be the temperature of the materials at mixing.

Table of the Quantity of *Real Potassa* in watery solutions of different *Specific Gravities*.

| Atoms of pot. water. | Potassa percent. by weight. | Potassa percent. by measure. | Specific gravity. | Congeealing point. | Boiling point. |
|----------------------|-----------------------------|------------------------------|-------------------|--------------------|----------------|
| 1 + 0 | 100 . . | 240 . . | 2,4 . . | unknown. | unknown. |
| 1 + 1 | 84 . . | 185 . . | 2,2 . . | 1000° . . | red heat. |
| 1 + 2 | 72,4 . . | 145 . . | 2,0 . . | 500° . . | 600° |
| 1 + 3 | 63,6 . . | 119 . . | 1,88 . . | 340° . . | 420° |
| 1 + 4 | 56,8 . . | 101 . . | 1,78 . . | 220° . . | 360° |
| 1 + 5 | 51,2 . . | 86 . . | 1,68 . . | 150° . . | 320° |
| 1 + 6 | 46,7 . . | 75 . . | 1,60 . . | 100° . . | 290° |
| 1 + 7 | 42,9 . . | 65 . . | 1,52 . . | 70° . . | 276° |
| 1 + 8 | 39,6 . . | 58 . . | 1,47 . . | 50° . . | 265° |
| 1 + 9 | 36,8 . . | 53 . . | 1,44 . . | 40° . . | 255° |
| 1 + 10 | 34,4 . . | 49 . . | 1,42 . . | | 246° |
| | 32,4 . . | 45 . . | 1,39 . . | | 240° |
| | 29,4 . . | 40 . . | 1,36 . . | | 234° |
| | 26,3 . . | 35 . . | 1,33 . . | | 229° |
| | 23,4 . . | 30 . . | 1,28 . . | | 224° |
| | 19,5 . . | 25 . . | 1,23 . . | | 220° |
| | 16,2 . . | 20 . . | 1,19 . . | | 218° |
| | 13, . . | 15 . . | 1,15 . . | | 215° |
| | 9,5 . . | 10 . . | 1,11 . . | | 214° |
| | 4,7 . . | 5 . . | 1,06 . . | | 213° |

Ingredients of the principal varieties of Potash of Commerce.

| | Potash. | Sulphate of potash. | Muriate of potash. | Insoluble residue. | Carbonic acid and water. | Total. |
|------------------------|---------|---------------------|--------------------|--------------------|--------------------------|--------|
| Potash of Russia . . . | 772 | 65 | 5 | 56 | 254 | 1152 |
| " America . . . | 857 | 154 | 20 | 2 | 119 | 1152 |
| American Pearl-ash . . | 754 | 80 | 4 | 6 | 308 | 1152 |
| Potash of Treves . . . | 720 | 165 | 44 | 24 | 199 | 1152 |
| " Dantzic . . . | 603 | 152 | 14 | 79 | 304 | 1152 |
| " Vosges . . . | 444 | 148 | 510 | 34 | 304 | 1440 |

Colour of Precipitates thrown down from Metallic Solutions, by various Re-agents.

| Metals. | Prussiates or Ferro-cyanates. | Tincture of Galls | Water impregnated with Sulphurated Hydrogen. | Hydro-Sulphurets. |
|--|--|--|--|----------------------------|
| Antimony | White | A white oxide merely from dilution. | Orange | Orange |
| Arsenic | White | Little change | Yellow | Yellow |
| Bismuth | White | Orange | Black | Black |
| Cadmium | White | No change | Orange | Orange |
| Cerium | White | Yellowish | | Brown, becoming deep green |
| Chromium | Green | Brown | | Green |
| Cobalt | Grass-green | Yellowish white | Not precipitated | Black |
| Columbium | Olive | Orange | | Chocolate |
| Copper (per-salts) | Bright reddish brown | Brownish | Black | Black |
| Gold | White | Solution turned green. Precipitate brown of reduced gold | Yellow | Yellow |
| Iridium | No precipitate. Colour discharged | No precipitate. Colour of solutions discharged | | |
| Iron { 1. Proto-salts 2. Per-salts. | White, changing to blue. Deep blue | No precipitate. Black | Not precipitated | Black |
| Lead | White | White | Black | Black |
| Manganese | White | No precipitate | Not precipitated | White |
| Mercury | White, changing to yellow | Orange yellow | Black | Brownish black |
| Molybdenum | Brown | Deep brown | Brown | |
| Nickel | Apple-green | Greyish white | Not precipitated | Black |
| Osmium | | Purple, changing to deep vivid blue | | |
| Palladium | Olive.* Deep orange† | | Dark brown | Dark brown |
| Platinum | No precipit. but an orange coloured one by pruss. of mercury | Dark green becoming paler | Precipitated in a metallic state | |
| Rhodium | No precipitate | | | No precipitate |
| Silver | White | Yellowish brown | Black | Black |
| Tellurium | No precipitate | Yellow | | Blackish |
| Tin | White | No precipitate | Brown | Black |
| Titanium | Reddish brown | Reddish brown | Not precipitated | Grass-green |
| Tungsten | | | | |
| Uranium | Blood-red | Chocolate | | Brownish yellow |
| Zinc | White | No precipitate | Yellow | White |

* Chenevix.

† Wollaston.

Specific gravity of Essential and Fat Oils.

| | |
|--------------------------------|--------|
| Oil of Cinnamon | 1,0439 |
| " " Cloves | 1,0363 |
| " " Lavender | 0,8938 |
| Spirit of Turpentine | 0,8697 |
| Linseed oil | 0,9403 |
| Poppy oil | 0,9288 |
| Oil of almonds | 0,9170 |
| Olive oil | 0,9153 |

The following estimate of different weights will be frequently useful in the laboratory.

| | Grains. |
|------------------------------|---------|
| Pound avoirdupoise | 7000, |
| Ounce " | 437,5 |
| Pound troy | 5760, |
| Ounce " | 480, |
| Gramme | 15,4063 |
| Decigramme | 1,5406 |
| Centigramme | 0,1540 |
| Milligramme | 0,0154* |

The following are useful estimates and comparisons of certain measures both linear and cubic, with the weights of the cubic measures added in grains of distilled water.

| | | |
|---|---------------|----------------------------|
| | Inches. | |
| Yard | 36, | |
| Metre | 39,37079 | |
| Deci-metre | 3,93708 | |
| Centi-metre | 0,39370 | |
| Milli-metre | 0,03937 | |
| The seconds pendulum vibrating at London 39,13929 | | |
| | | |
| | Cubic Inches. | Grains of distilled water. |
| Gallon | 277,274 | 70000, |
| Pint | 34,65925 | 8750, |
| Cubic inch | 1, | 252,453 |
| Litre | 61,02525 | 15406,312 |
| Deci-litre | 6,10252 | 1540,631 |
| Centi-litre | 0,61025 | 154,063 |
| Milli-litre | 0,06102 | 15,406* |

Table of solutions which may be used in baths when temperatures above 212° are required.

| | |
|--|------|
| Bitartrate of Potassa boils at | 214° |
| Alum | 220 |
| Borax | 222 |
| Common Salt | 224 |
| Nitre | 238 |
| Rochelle Salt | 240* |

* Faraday's Chem. Manip.

GENERAL INDEX.

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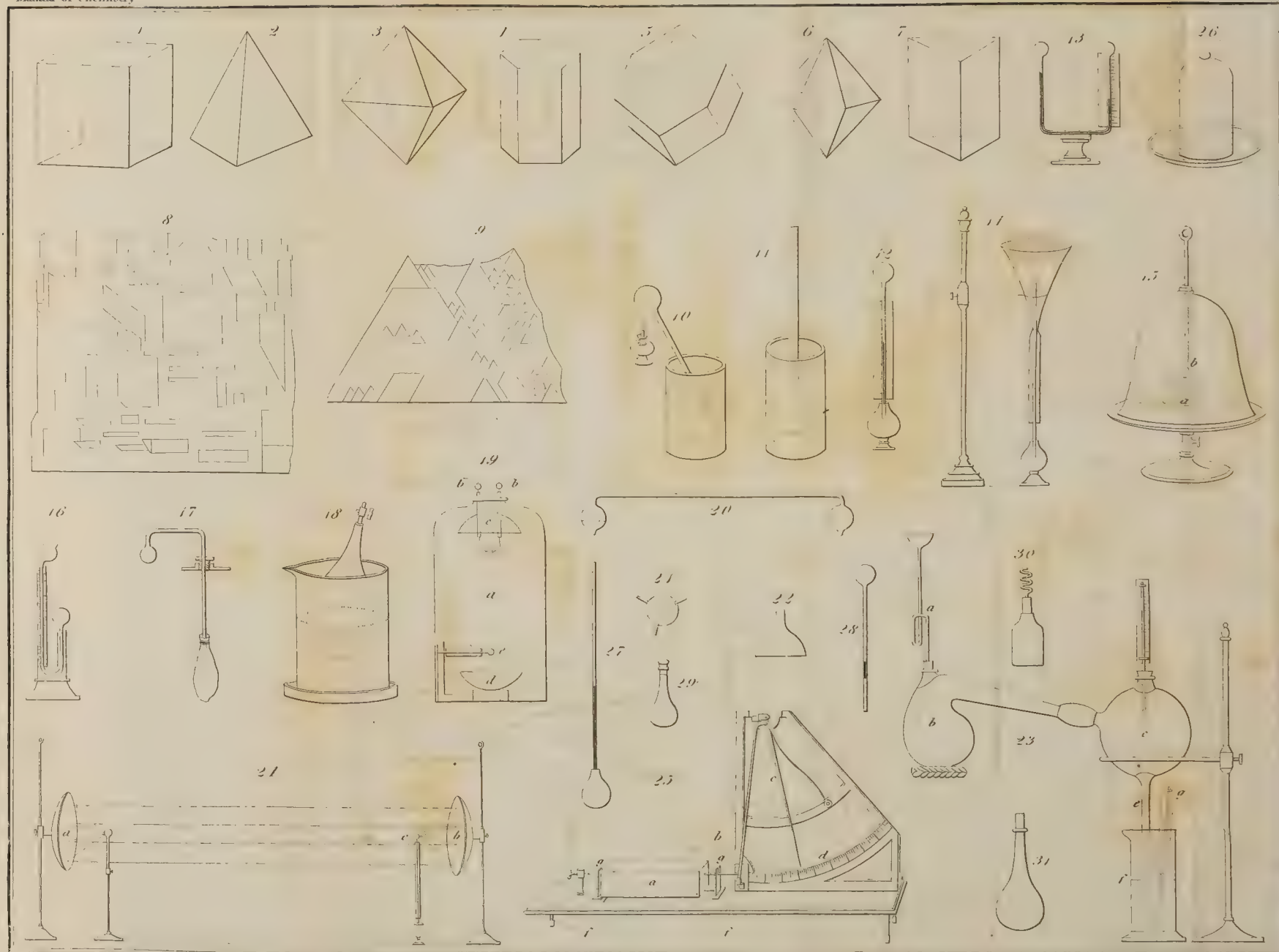
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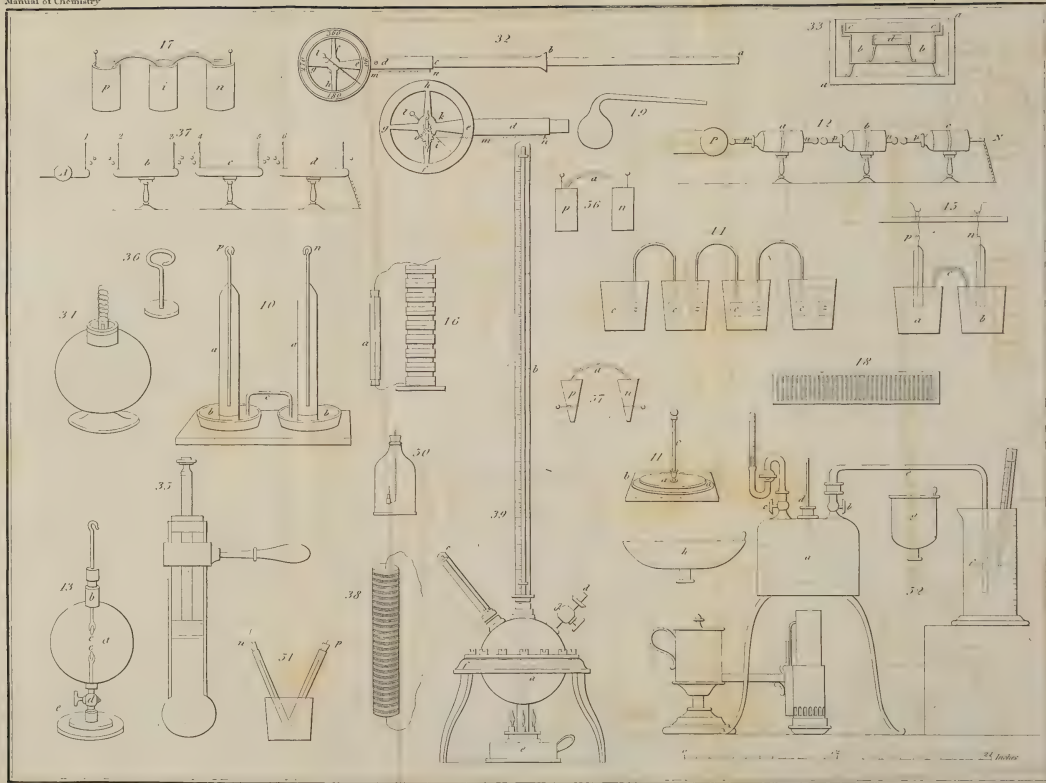
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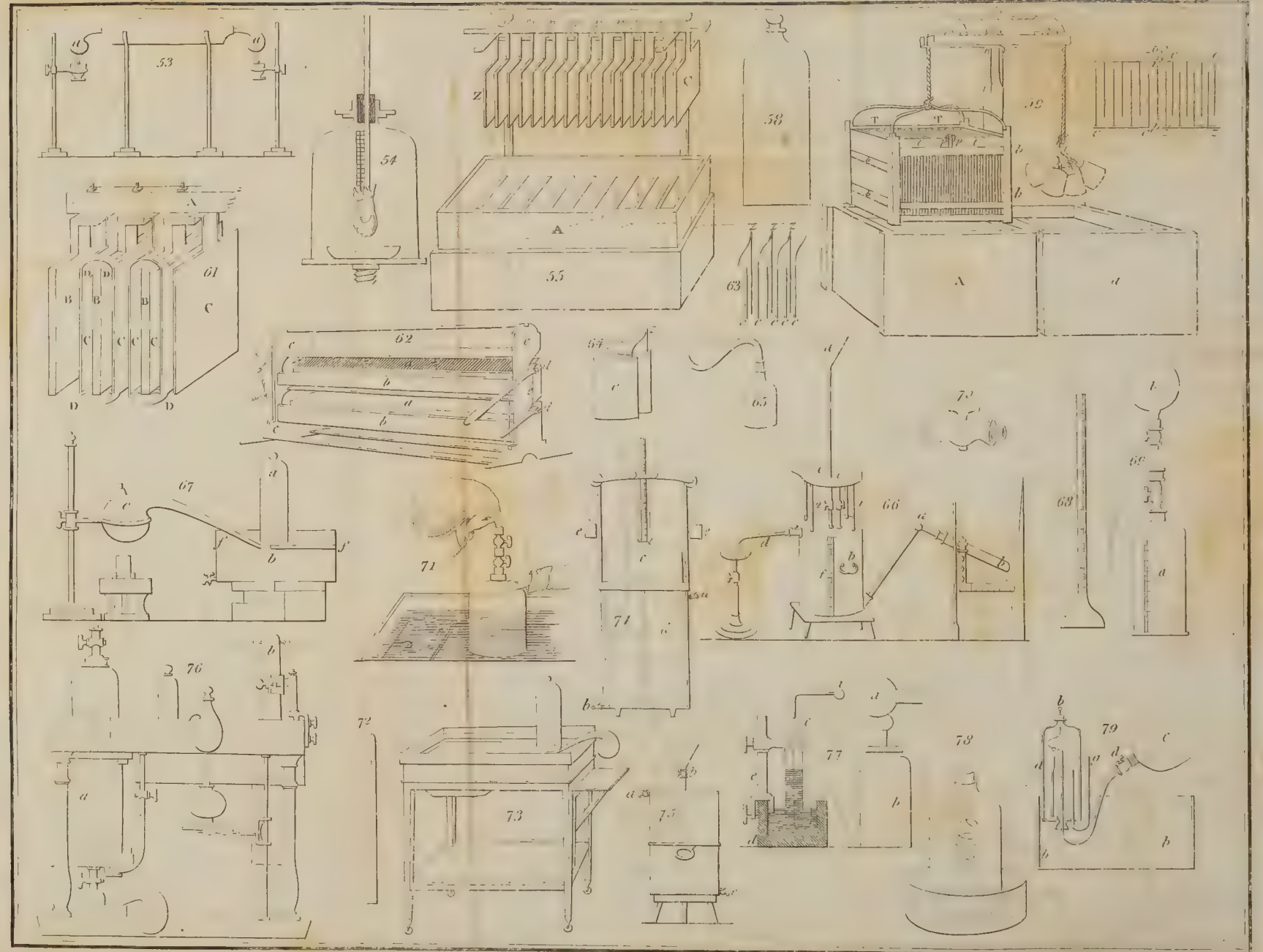
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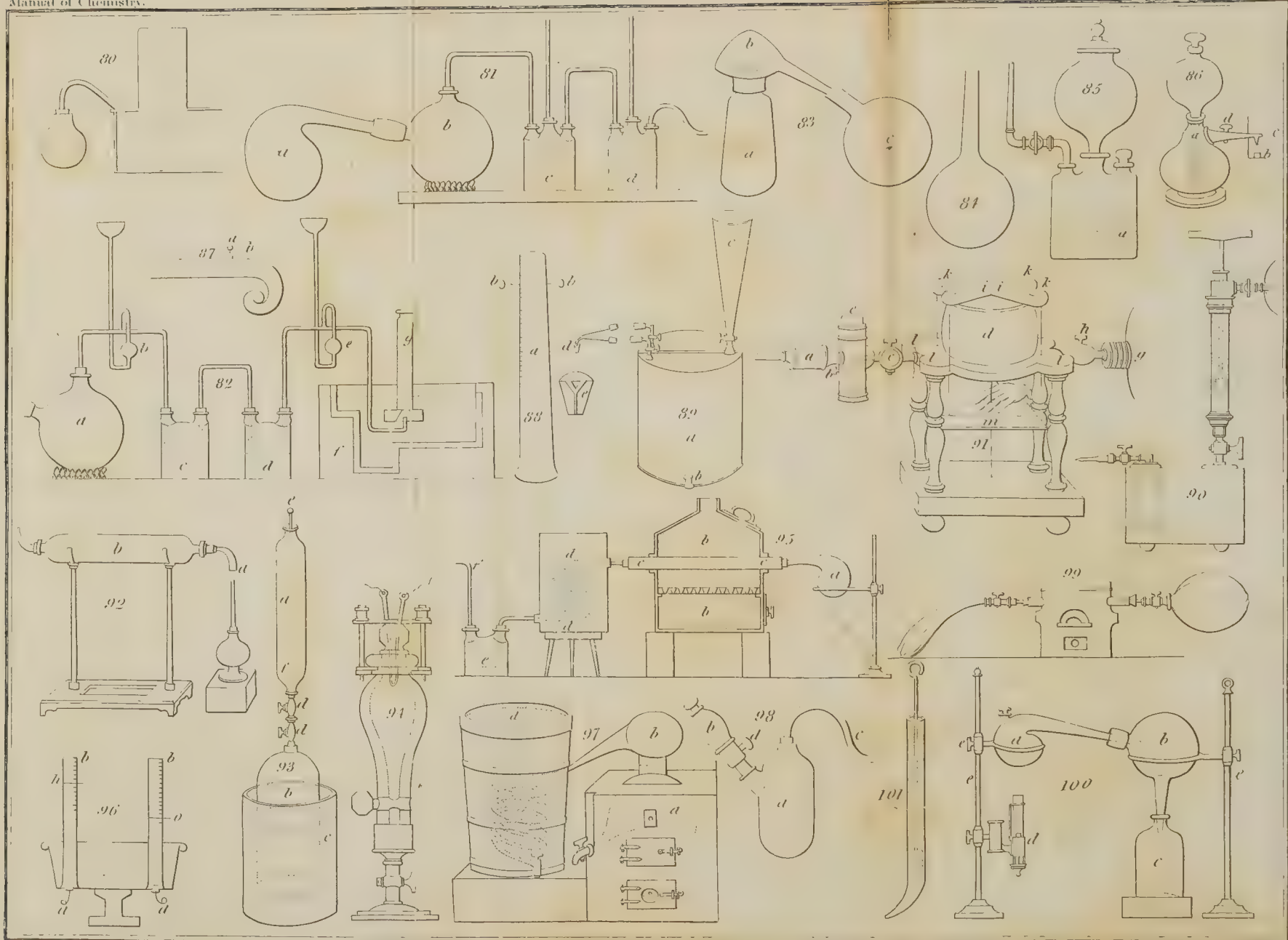
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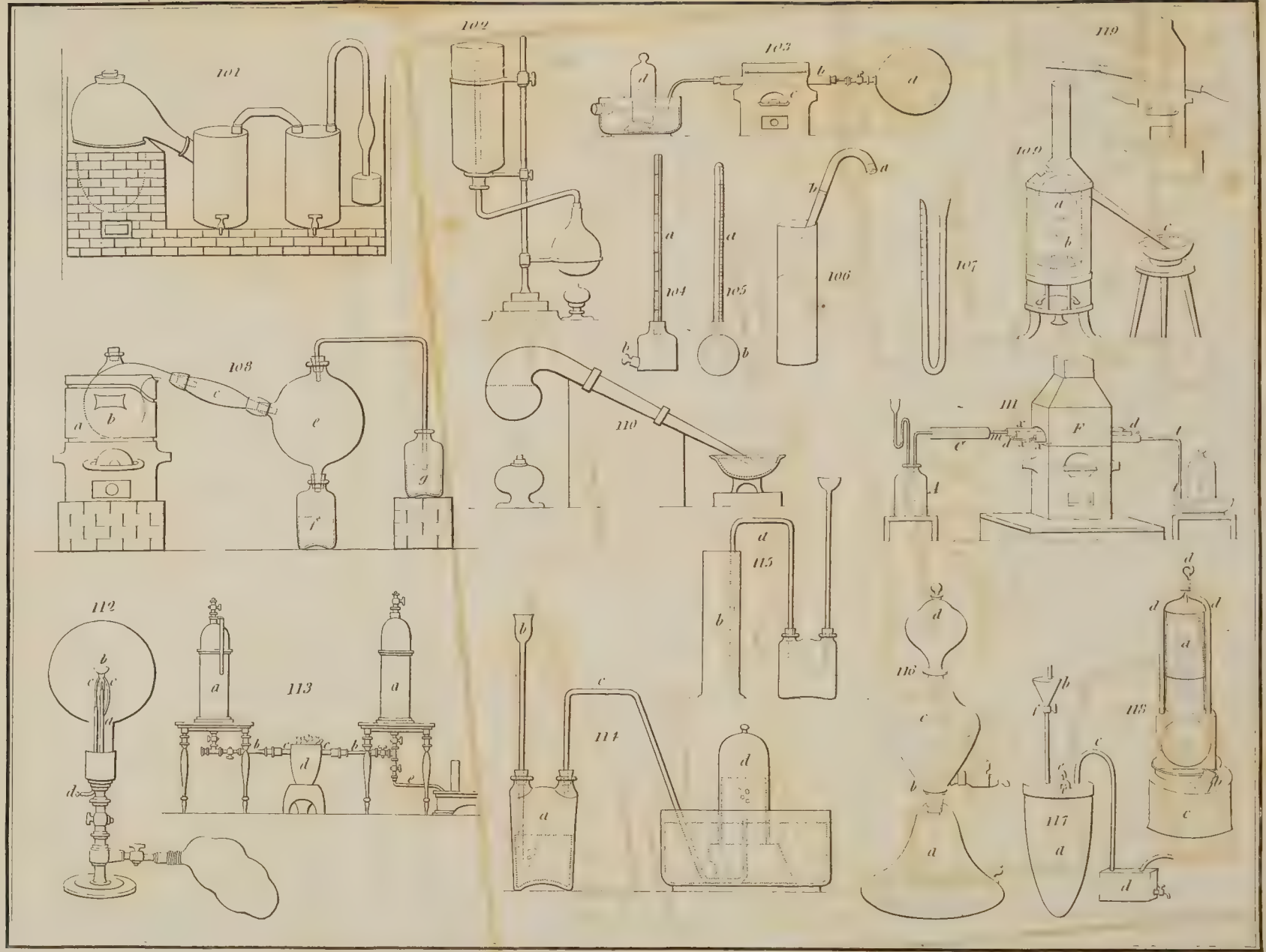




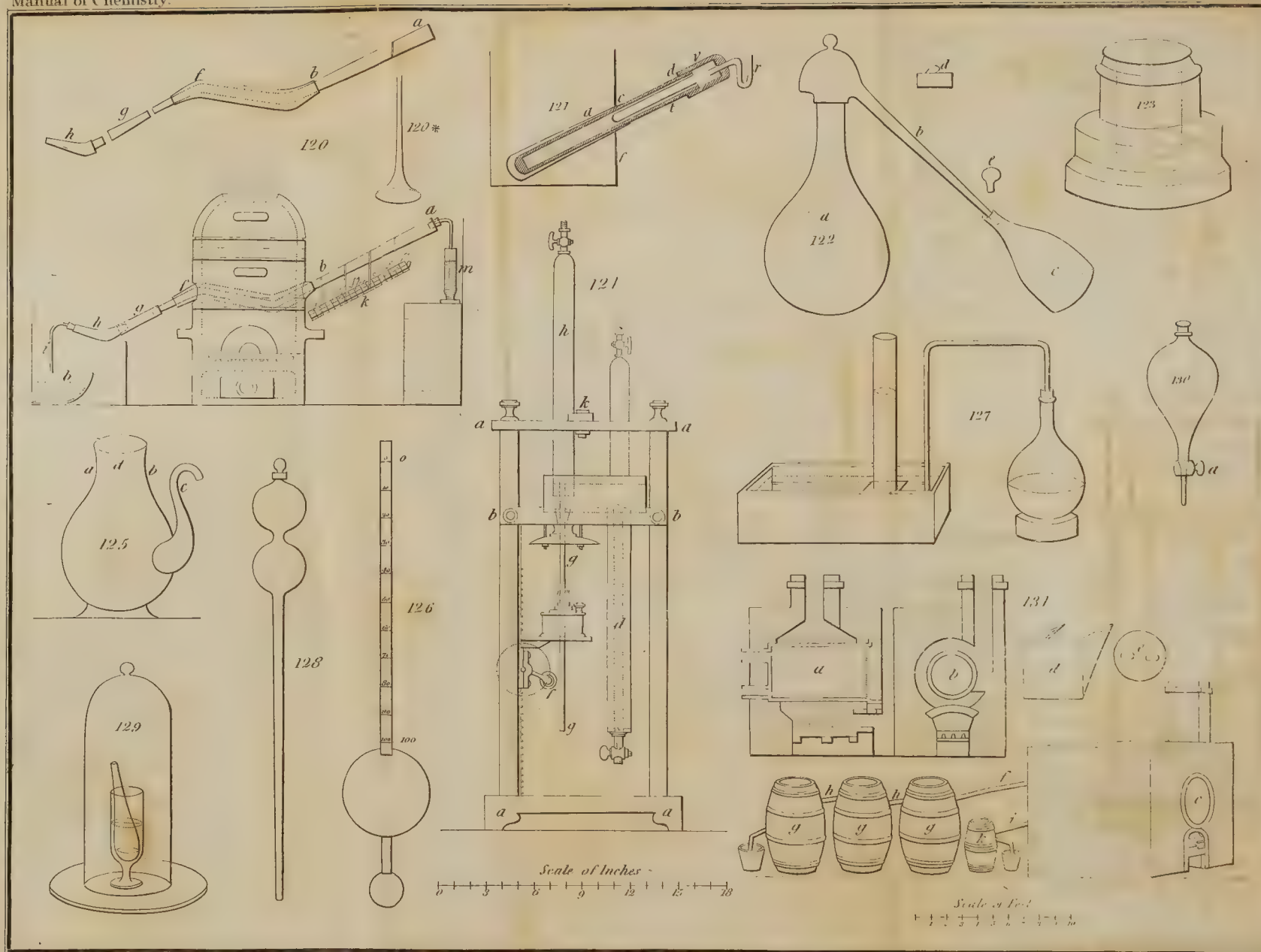












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